

Atlantic Richfield Company

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June 14, 2013

Mr. Steven Way
On-Scene Coordinator
Emergency Response Program (8EPR-SA)
U.S. EPA Region 8
1595 Wynkoop Street
Denver, CO 80202-1129

RE:

St. Louis Tunnel Discharge Source Mine Water Treatability Study

Work Plan Addendum

Rico-Argentine Mine Site – Rico Tunnels, Operable Unit OU01

Dolores County, Colorado

Dear Mr. Way:

On behalf of Atlantic Richfield Company (Atlantic Richfield), please find enclosed the *St. Louis Tunnel Discharge Source Mine Water Treatability Study Work Plan Addendum* (Work Plan Addendum) prepared for the Rico-Argentine Mine Site (site). This Work Plan Addendum notifies the U.S. Environmental Protection Agency, Region 8, (U.S. EPA) of Atlantic Richfield's plans for continuing a treatability study to evaluate the potential to reduce metal loadings at the St. Louis Tunnel discharge by treating source water generated in the Blaine-Argentine mine workings. Atlantic Richfield requests U.S. EPA's approval of this Work Plan Addendum pursuant to requirements in Task F – Water Treatment System Analysis and Design / Subtask F2 – Treatment System Conceptual Designs and Additional Investigations of the Remedial Action Work Plan accompanying the Unilateral Administrative Order for Removal Action, Rico-Argentine Site, Dolores County, U.S. EPA Region 8, dated March 9, 2011 (Docket No. 08-2011-0005).

If you have any questions regarding this Work Plan Addendum, please feel free to contact me at (714) 228-6770 or via e-mail at Anthony.Brown@bp.com.

Sincerely, Carry a. Bru

Tony Brown

Project Manager Mining Atlantic Richfield Company

Enclosures: St. Louis Tunnel Discharge Source Mine Water Treatability Study

Work Plan Addendum

cc: Ronald Halsey, Atlantic Richfield Company (via e-mail)

Terry Moore, Atlantic Richfield Company (via e-mail)

Sheila D'Cruz, Atlantic Richfield Company (via e-mail)



Mr. Steven Way U.S. EPA Region 8 June 14, 2013 Page 2 of 2

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ST. LOUIS TUNNEL DISCHARGE SOURCE MINE WATER TREATABILITY STUDY WORK PLAN ADDENDUM

Rico-Argentine Mine Site – Rico Tunnels
Operable Unit OU01
Dolores County, Colorado

Prepared for:
Atlantic Richfield
La Palma, California

Prepared by:

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June 2013

Project No. SA11161313



TABLE OF CONTENTS

		Pa	ge				
1.0	INTRO	DUCTION					
	1.1 1.2	HEALTH, SAFETY, SECURITY, AND ENVIRONMENT EXPECTATIONS					
2.0	BACK 2.1	CKGROUNDPREVIOUS TREATABILITY STUDY RESULTS					
3.0	PURP	OSE AND OBJECTIVES6					
4.0	PROJE	ECT OVERVIEW	7				
5.0	PROJE 5.1	ECT PHASESPRE-INJECTION	8 8				
		5.1.2 Injection Test Mobilization and System Construction	11				
	5.2	INJECTION	11				
		5.2.2 Continuous Tracer Injection					
	5.3	POST-INJECTION	18				
		5.3.1 Post-Injection Monitoring					
6.0	IMPLE	MENTATION SCHEDULE					
7.0			20				
8.0	REPO	RTING	20				
9.0	REFE	RENCES	21				
		TABLES					
Table 1 Table 2		Analytical and Field Monitoring Results, 2012 Baseline Samples Summary of Sampling and Analysis Program, 2013 Injection Test					
		FIGURES					
Figure 1 Figure 2 Figure 3 Figure 4		Site Location Map Rico Mine Site Mine Workings Layout Process Flow Diagram					
APPENDIX							
Appendix A		St. Louis Tunnel Discharge Source Mine Water Treatability Study Quality Assurance Project Plan					



LIST OF ACRONYMS

°C degrees Celsius °F degrees Fahrenheit

AMEC Environment & Infrastructure, Inc. **AMEC**

Atlantic Richfield Company Atlantic Richfield calcite; calcium carbonate CaCO₃

CDRMS Colorado Division of Reclamation, Mining and Safety

Comprehensive Environmental Response, Compensation and Liability Act **CERCLA**

CO2 carbon dioxide DO dissolved oxygen data quality objective DQO gram per liter g/L

gallon per minute gpm

hydraulic residence time HRT

HSSE Health, Safety, Security and Environment

ion specific electrode ISE K₂CO₃ potassium carbonate lithium chloride LiCI mg/L milligram per liter sodium bromide NaBr

Na₂CO₃ soda ash: sodium carbonate

NaHCO₃ sodium bicarbonate NaOH sodium hydroxide

northwest NW

ORP oxidation reduction potential **QAPP Quality Assurance Project Plan RAWP** Removal Action Work Plan RTD residence time distribution SAP Sampling and Analysis Plan

SE southeast

site Rico-Argentine Mine Site - Rico Tunnels, Operable Unit OU01, Dolores

County, Colorado

SOP Standard Operating Procedure

standard units su

Task Safety Environmental Analysis TSEA UAO **Unilateral Administrative Order**

U.S. EPA U.S. Environmental Protection Agency

St. Louis Tunnel Discharge Source Mine Water Treatability Study Work Plan

Work Plan (Atlantic Richfield, 2012)



ST. LOUIS TUNNEL DISCHARGE SOURCE MINE WATER TREATABILITY STUDY WORK PLAN ADDENDUM

Rico-Argentine Mine Site – Rico Tunnels Operable Unit OU01 Dolores County, Colorado

1.0 INTRODUCTION

This St. Louis Tunnel Discharge Source Mine Water Treatability Study Work Plan Addendum (Work Plan Addendum) has been prepared by AMEC Environment & Infrastructure, Inc. (AMEC) on behalf of Atlantic Richfield Company (Atlantic Richfield) to describe the scope of work to be conducted to evaluate the treatability of water within the underground workings of the Rico-Argentine Mine Site – Rico Tunnels, Operable Unit OU01 (site). The site is located in the San Juan Mountains of southwestern Colorado, just north of the Town of Rico in Dolores County, Colorado (Figure 1). The site consists of the St. Louis Tunnel and associated complex of underground mine workings, as well as a series of settling ponds. A general site layout is presented in Figure 2.

The activities described in this Work Plan Addendum are being conducted pursuant to the *Unilateral Administrative Order for Removal Action (UAO), Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) Docket No. 08-20011-0005*, effective March 23, 2011 (UAO; U.S. Environmental Protection Agency [EPA], 2011b), and the associated Removal Action Work Plan (RAWP) dated March 9, 2011, in connection with the site (U.S. EPA, 2011a).

The work described in this Work Plan Addendum is a continuation of the treatability study that was conducted in 2012 (AMEC, 2013). Between September and November 2012, Atlantic Richfield evaluated in-situ chemical treatment as a method for reducing metals concentrations in the St. Louis Tunnel discharge and found that concentrations of many metals can be substantially reduced with this approach. This Work Plan Addendum is an extension of the previous *St. Louis Tunnel Discharge Source Mine Water Treatability Study Work Plan* (Work Plan; Atlantic Richfield, 2012) and describes field work that will be conducted during the 2013 field season to evaluate treatment approaches and site conditions that were not tested in 2012. Alkaline solutions will be injected at higher dosages, for a longer duration, during a different part of the field season having higher flows and metal concentrations, as compared to the testing that was completed in 2012. The overall treatment approach has the potential to reduce metals concentrations discharging from the St. Louis Tunnel and could subsequently



reduce the water treatment design capacity and solids handling and disposal requirements of any final remedy treatment system that is implemented for reducing metal loads to the Dolores River.

1.1 HEALTH, SAFETY, SECURITY, AND ENVIRONMENT EXPECTATIONS

All tasks described herein will be performed in accordance with the Site Specific Health and Safety Plan as well as Task Specific Health, Safety, Security, and Environment (HSSE) Plans prepared by Atlantic Richfield's contractors. The appropriate Risk Assessments, Task Safety Environmental Analysis (TSEAs), Standard Operating Procedures (SOPs), and permits will be completed prior to initiating any of the work described herein.

All underground work will be performed by the United States Environmental Protection Agency (U.S. EPA) and their contractor personnel. Under no circumstances will Atlantic Richfield's contractors and/or lower tier subcontractors will be allowed to break the plane of the related mine portals. The U.S. EPA and its contractors are responsible for managing the health and safety of their personnel and subcontractors.

1.2 COORDINATION AND RESPONSIBILITIES

The project team for the 517 injection test will consist of key personnel from Atlantic Richfield, U.S. EPA, and the Colorado Division of Reclamation, Mining and Safety (CDRMS), as well as its contractor personnel. The treatability study tasks will be divided between the U.S. EPA and its contractor personnel providing in-tunnel support and Atlantic Richfield providing equipment and contract personnel for out-of mine support. Detailed roles and responsibilities will be reviewed with the entire team prior to the start of work. The team will also be informed of injection test results as described in Section 8.

This treatability study has been designed to minimize the amount of underground and in-tunnel work required for implementation. The bulk of the equipment necessary to implement the treatability study will be located at the surface, outside of the portals of the Blaine and 517 Shaft Access Tunnels.

2.0 BACKGROUND

The St. Louis Tunnel portal drains historical mine workings that extend several thousand feet into Telescope Mountain to the north and Dolores Mountain to the southeast (SE) (Figure 3). The mine workings to the northeast of the site (Pigeon, Logan, Wellington, and Mountain Springs mines) are or were hydraulically connected to the St. Louis Tunnel via the Northwest (NW) Cross-cut. The workings in the southeastern portion of the site (Argentine, Blaine,



Blackhawk, and other mines, collectively referred to herein as the Blaine-Argentine mine workings) are hydraulically connected to the St. Louis Tunnel via the SE Cross-cut (Figure 3). The Blaine Tunnel and 517 Shaft provide access to the underground mine workings approximately 500 vertical feet above the St. Louis Tunnel level. Various interconnected "vertical" mine workings (shafts, raises, winzes, inclines, drifts, adits) and mined-out stopes provide inferred opportunities for hydraulic connection of flows in and through the "horizontal" mine workings (i.e., the Blaine-Argentine mine workings and 517 Shaft) at the 100 level and the underlying 200, 300, and 400 levels to the SE Cross-cut at the 500 level. These interconnected workings direct infiltrating precipitation (primarily snowmelt) as groundwater to the St. Louis Tunnel. As the groundwater travels through the workings, oxidation of mineralized rock increases the metal concentrations in the mine water.

In 2011, water sampling and tracer tests were conducted in the Rico-Argentine mine system (URS, 2012). Mine water in the 517 Shaft had a pH of 2.7 standard units (su), with high concentrations of many metals (URS, 2012). Tracer test results indicated that there is dispersion, storage, and/or blockage of flow within the mine workings. The collapsed section of the adit near the St. Louis Tunnel portal may impede flow, and in addition, tracers may have a long residence time in the 517 Shaft mine water pool after injection and before flowing into the SE Cross-cut. URS (2012) made several recommendations for further investigation to characterize source water from the Blaine Tunnel, identify seasonal variations in water quality, and provide further characterization of mine water flows. Many of these recommendations were implemented in 2012.

2.1 PREVIOUS TREATABILITY STUDY RESULTS

The 2012 treatability study evaluated chemical injection to the 517 Shaft as a method for reducing metals concentrations at the St. Louis Tunnel discharge. Test activities included tracer studies to characterize flows between the 517 Shaft and the St. Louis Tunnel discharge and injection of alkaline solutions to the 517 Shaft to evaluate treatability of mine water. The 2012 treatability study was performed according to the Work Plan (Atlantic Richfield, 2012), and results are described in the *St. Louis Tunnel Discharge Source Mine Water Treatability Study Completion Report* (AMEC, 2013). The following paragraphs briefly summarize the 2012 treatability study.

The 2012 treatability study was conducted over 42 days between September and November 2012. Alkaline solutions were injected to the 517 Shaft to increase alkalinity and pH, with the goal of precipitating metals within the mine workings and thus reducing effluent concentrations at the St. Louis Tunnel discharge. Potassium carbonate (K₂CO₃) was injected for the entire test, and sodium hydroxide (NaOH) was injected during the final week. Injection totals were



as follows: 22,700 gallons of 23.5 percent (%) K₂CO₃ solution; 626,800 gallons of Silver Creek water (injected as carrier water due to low flows through the mine workings); and 330 gallons of 25% NaOH solution.

In the 517 Shaft mine water pool, injection of K_2CO_3 and NaOH increased the pH and alkalinity and decreased metals concentrations. The total alkalinity increased from approximately 30 milligrams per liter (mg/L) as calcium carbonate (CaCO₃) to 3,000 mg/L as CaCO₃ with injection of K_2CO_3 . Further increase of alkalinity was minor with injection of NaOH, although the form of alkalinity shifted from predominately bicarbonate to carbonate. The pH in the 517 Shaft increased from 6.1 su to as high as 10.6 su with injection of K_2CO_3 and as high as 11.7 su with the addition of NaOH. Total metals concentrations in the 517 Shaft were reduced by about 90% with injection of K_2CO_3 and by about 95% with injection of NaOH with K_2CO_3 . Dissolved concentrations of many metals in the 517 Shaft were reduced by 90% or more during injection of K_2CO_3 and to below reporting limits during injection of NaOH with K_2CO_3 .

At the St. Louis Tunnel discharge sampling location (DR-3A; Figure 3), the pH increases were limited (up to 0.4 su during injection of NaOH with K₂CO₃) due to dilution and neutralization within the flow system between the 517 Shaft and DR-3A. During the first two weeks of injection, total bicarbonate alkalinity at DR-3A increased by 22% (from 90 to 110 mg/L as CaCO₃). Increased doses of K₂CO₃ and injection of NaOH did not further increase alkalinity at DR-3A. Zinc and cadmium concentrations at DR-3A decreased by about 40% and the manganese concentration decreased by up to 25%. The highest reductions occurred during the first two weeks of K₂CO₃ injection; later injection of NaOH did not substantially improve metals removal at DR-3A.

These results indicate that injection of K₂CO₃ to the 517 Shaft provided sufficient excess alkalinity to reduce concentrations of zinc, cadmium, manganese, and other metals at the St. Louis Tunnel discharge. These reductions at DR-3A may have been due to the combined effects of reduced dissolved metals loading from the 517 Shaft mine water pool and carryover of alkalinity to the St. Louis tunnel and subsequent precipitation of metals in the mine water pool behind the collapsed St. Louis Tunnel portal. The subsequent injection of NaOH was insufficient to further increase the alkalinity and pH or to further decrease metals concentrations at DR-3A. The injection was suspended before higher rates could be tested, due to the onset of winter weather conditions.

Although the pH at DR-3A increased in response to injection of K₂CO₃, the overall increases above the pre-injection pH were relatively small, indicating that the alkaline materials and the high pH generated in the 517 Shaft were diluted and neutralized during transport through the



mine workings. The alkalinity added during K₂CO₃ injection was not sufficient to satisfy the carbonate alkalinity demand in the mine workings between the 517 Shaft and DR-3A, largely from the flows from the NW Cross-cut. The loss of alkalinity was most likely due to softening mechanisms, primarily the precipitation of calcium as CaCO₃.

Tracer tests during the 2012 study confirmed the hydraulic connection between the 517 Shaft and the St. Louis Tunnel discharge and provided information about the hydraulic characteristics of the system. Tracer test results indicated that the mean hydraulic residence time (HRT) of the system was approximately 11 days. Lithium, which was continuously injected for the first 12 days, approached equilibrium concentrations at DR-3A, but potassium appeared to be non-conservative at high pH during injection of NaOH. NaOH was not injected long enough to reach equilibrium sodium concentrations at the St. Lois Tunnel discharge. Under the conditions of the 2012 tracer tests, tracers injected to the 517 Shaft were slow to appear at DR-3A in comparison to the previous tracer test conducted in October 2011. URS (2012) reported that tracers injected to the 517 Shaft first appeared at DR-3A in about 15 hours, while concentrations of lithium and fluorescein peaked at about 21 and 37 hours, respectively.

The results of the 2012 injection test suggested that injection of alkaline solutions in the 517 Shaft is a potential method for mitigating metals concentrations at the St. Louis Tunnel discharge, but additional information is needed before this method can be recommended or implemented. Based on the 2012 findings, recommendations are made for additional treatability testing to improve metals removal. AMEC (2013) recommends the following:

- Higher doses of NaOH should be injected to the 517 Shaft, without concurrent addition of K₂CO₃. Sufficient doses at the 517 Shaft will treat mine water throughout the system: the 517 Shaft, the SE Cross-cut, the NW Cross-cut, and the mine water pool behind the collapsed St, Louis Tunnel adit. Injection of NaOH alone will increase pH and alkalinity, while reducing losses of carbonate alkalinity to softening (i.e., precipitation of CaCO₃).
- Injection testing should be conducted for a longer duration to allow the system to approach steady state conditions. This will allow more accurate evaluation of tracer test results and allow a determination of the sustainability of this approach.
- Injection testing should be completed under higher flow conditions, such as the
 higher flows and attending metal concentrations, that are expected during spring
 and early summer runoff and while mine water is flowing from the Blaine Tunnel to
 the 517 Shaft. Testing under these conditions will yield information about the
 effectiveness of treatment during periods of higher flows and higher metals loading.



Additional tracer testing and geochemical modeling should be conducted to better
characterize flow characteristics of the system. These additional efforts will provide
information that is needed to effectively design a full-scale system and to develop
models that can be used to predict removals of metals under different operating
conditions, based on readily measurable quantities (i.e., flow and concentrations at
DR-3A; flow over the Blaine Tunnel weir; and water levels and concentrations in the
517 Shaft). These analyses may help to understand precipitation of other minerals
and sludges, and the potential effects on hydraulic properties of the workings.

Results of the 2012 injection test are described in further detail by AMEC (2013).

3.0 PURPOSE AND OBJECTIVES

The 2013 injection test as described in this Work Plan Addendum will be a follow-on to the 2012 injection test and will implement the recommendations of the 2012 Completion Report (AMEC, 2013). The purpose of the 2013 Treatability Study is to further evaluate chemical injection to the 517 Shaft as a method for reducing concentrations of metals in the St. Louis Tunnel discharge. Tracer testing will also provide additional information about the hydraulic characteristics of the system, the flow rate through the 517 Shaft, and information on the contribution of metal loads from the NW Cross-cut to the St. Louis Tunnel discharge.

The 2013 injection test will be different from the 2012 injection test in several important aspects:

- Injection of higher doses of a different alkaline solution (25% NaOH, rather than K₂CO₃ as in 2012) as the primary method of increasing pH and alkalinity;
- Operation for a longer duration than the 2012 injection test, to allow equilibrium concentrations to be established at the St. Louis Tunnel discharge;
- Evaluation of the method for treating higher flows and consequential metals loadings expected during early summer runoff; and
- No potential impacts from reduced flows or chemical loading due to dewatering of the Blaine Tunnel.

These features of the 2013 injection test incorporate many of the recommendations based on the findings of the 2012 injection test results.

This Work Plan Addendum describes the activities that will be completed as a continuation of the 2012 treatability study and tracer tests. The primary objective of the proposed work is to further evaluate injection of alkaline solutions to the 517 Shaft as a sustainable method for



mitigating metals loading at the St. Louis Tunnel discharge. The specific objectives of the proposed injection testing are as follows:

- Determine changes in metals concentrations and other water quality parameters at the St. Louis Tunnel discharge in response to injection of varied doses of alkaline solutions to the 517 Shaft;
- Evaluate the residence time distribution of water flowing between the 517 Shaft and the St. Louis Tunnel discharge using a short-term injection of conservative tracer; and
- Estimate the mine water flow rates (i.e., flow through the 517 Shaft into the St. Louis Tunnel and flow from the NW Cross-cut into the St. Louis Tunnel) by achieving steady-state effluent concentrations of a continuously-injected conservative tracer.
- Estimate the volume of sludge being precipitated in the workings.

Although the completion of this work will be limited by seasonal variations in flow rates and metals loading that have been observed at the St. Louis Tunnel discharge, the treatability and tracer test results will support the assessment of the potential viability of this treatment approach. Treatability test results from 2013 will be integrated with earlier results (2011 tracer tests [URS, 2012], 2012 injection test [AMEC, 2013], and 2012 tracer tests [AMEC, 2013]) to further assess the feasibility of this remediation approach and form a basis for potential design and full-scale implementation of this treatment method at the site.

4.0 PROJECT OVERVIEW

To meet the treatability study and tracer test objectives, AMEC has organized the proposed field work into the following three phases that will be implemented sequentially during the 2013 field season:

- Pre-Injection Phase This initial phase will include mobilization; geophysical characterization in the 517 Shaft to document conditions in the 517 Shaft during spring run-off; injection system construction and testing; and baseline water sampling to determine initial geochemical conditions.
- 2. Injection Phase After test equipment has been set up and tested, and baseline conditions have been established, injection of alkaline solutions to the 517 Shaft will commence. The primary injection solution will be 25% NaOH, which will increase pH and alkalinity in the system. The injected sodium ion will provide a continuously injected conservative tracer, and at least one short term (pulse injection) tracer test will be completed. A constant injection rate will be maintained until steady state sodium concentrations are achieved at DR-3A (St. Louis Tunnel)



- discharge). Monitoring and sampling will be conducted to evaluate changes in geochemical conditions in the 517 Shaft and at DR-3A.
- 3. Post-injection Phase After completing injections, additional post-injection sampling and field monitoring will be conducted to monitor the return to baseline geochemical conditions, and demobilization tasks will be completed.

Specific tasks that will be completed and additional details for each of these three phases are described further in the following section. To generate data of acceptable quality that will meet the objectives of this proposed work, the 2013 field work will follow the Sampling and Analysis Plan (SAP) that was included as Appendix A of the Work Plan (Atlantic Richfield, 2012), and with the Mine Source Water Treatability Study Quality Assurance Project Plan (QAPP) included as Appendix A of this Work Plan Addendum. Together, the SAP and QAPP address field monitoring methods, sample collection, test procedures and data quality. The sampling and analysis program for all phases of the 2013 work, including the proposed sample frequency, sampling methods, and analyses, is outlined in Table 2. Standard Operating Procedures (SOPs), including those that have been revised or added to those presented in the Work Plan (Atlantic Richfield, 2012), are included with the QAPP in Appendix A of this Work Plan Addendum.

5.0 PROJECT PHASES

This section describes the major components and rationale for each component of the three project phases. For each phase of the study, the scope, methods and data quality objectives (DQOs) are discussed. The schedule for each phase of the study is provided in Section 6.0.

5.1 PRE-INJECTION

The pre-injection phase of the proposed work will consist of further geophysical characterization of the 517 Shaft, injection test mobilization, system construction, and baseline sampling. This phase will be completed before any injection activities.

5.1.1 Geophysical Survey of 517 Shaft

Further geophysical characterization of the 517 Shaft will be conducted to document conditions in the shaft during spring run-off, when snowmelt and surface water flow rates are anticipated to be at their annual peak. This characterization work will utilize geophysical methods to evaluate the condition of the 517 Shaft and to characterize the water quality and flow in the flooded portion of the shaft. The geophysical survey will investigate mine water flows in and through the shaft, stratification of water quality parameters, and the geometry of the shaft. Results will be used to support the 2013 injection test.



A geophysical survey that was conducted in September, 2012 included downhole video of the shaft, a vertical log of water quality parameters, vertical flow velocity measurements in the submerged portion of the shaft, and collection of discrete water samples near the water surface. This work was performed during the first week of September 2012, when groundwater infiltration into the shaft was anticipated to be low, and before mine water was pumped from the Blaine Tunnel to the 517 Shaft to facilitate the Blaine Tunnel rehabilitation work. Results of the 2012 survey suggest that the 517 Shaft has a depth of approximately 623 feet (as measured with a small diameter logging probe) and intercepts as many as six different levels within the mine. At the time of that survey, a water column of approximately 171 feet was present in the bottom of the shaft.

The lessons learned during the 2012 geophysical characterization will enhance the 2013 geophysical characterization by providing improved data quality and greater data collection capabilities. The following methods will be used for the 2013 geophysical survey of the 517 Shaft:

- A downhole video camera with full pan and tilt capabilities and supplemental lighting.
- A submersible water quality tool with data logging capabilities will be deployed into the 517 Shaft to develop a vertical water quality profile in the submerged portion of the shaft. Pressure/depth, temperature, conductivity, dissolved oxygen (DO), pH, and oxidation reduction potential (ORP) will be measured.
- A sonar system will be deployed into the 517 Shaft to develop a three-dimensional image of the submerged portion of the shaft. This method will avoid limitations of video logging caused by turbidity in the mine water.
- A corehole dynamic flow meter and a colloidal borescope will be deployed to measure vertical and horizontal flow velocities, respectively.
- Depth-discrete water samples will be collected at several depths in the shaft using a Bennett submersible piston sample pump or a bailer. The number and location of samples will be dependent on the results of water quality measurements in the shaft and other geophysical observations.

AMEC, with support from Anderson Engineering Company Inc. (AECI), will lead the 517 Shaft geophysical characterization efforts. AMEC will subcontract Layne Christensen (Layne) from Golden, Colorado to perform the geophysical characterization. The U.S. EPA and their contractor personnel will provide in-tunnel support.



5.1.2 Injection Test Mobilization and System Construction

All materials and supplies will be shipped to and received at the site, and all components of the injection system will be constructed, checked, and tested. The system will be constructed by AECI and its subcontractors, with design and oversight by AMEC. System construction and installation will include external components (outside the 517 Shaft Access Tunnel, to be completed by Atlantic Richfield's contractors) and components that will be installed inside the 517 Shaft Access Tunnel (to be completed by U.S. EPA and their contractor personnel).

The injection system will be similar to the system that was used in 2012, with modifications to improve system reliability based on findings from the 2012 treatability study. The system will include the following general components as presented in the generalized process flow diagram for the treatability study system (Figure 4).

- Double wall epoxy coated steel chemical storage tanks (with a capacity of 10,000-gallons) for concentrated chemical injection solutions;
- Fluid transfer lines for chemical transfer:
- Injection pumps;
- Injection lines from the injection pumps to mine water in the 517 Shaft;
- Flow meter and flow totalizer on injection lines;
- · Secondary containment for the injection pumps, and injection lines;
- Water quality sonde probe submerged in the 517 Shaft mine water for continuous monitoring of pH, temperature, conductivity, and ORP;
- Electrical connections and generator power supply; and
- Provision for air injection if needed.

To maintain flexibility of operation, the system will include components for storage and injection of NaOH and K₂CO₃ solutions. The system will initially be constructed for storage and injection of 25% NaOH solution; components for storage and injection of K₂CO₃ (optional components as shown in Figure 4) will be added if necessary. Components for injection of water from Silver Creek (pump and injection line) will also be added to the system, if needed. Decision criteria for use of each of these systems are included in Section 5.2.

Mobilization will also include delivery of the initial chemical injection solution (25% NaOH) to the site. The system will be wet tested with clean water and commissioned prior to startup.



5.1.3 Baseline Sampling

Baseline water samples will be collected from the Blaine Tunnel, from the 517 Shaft, and from the St. Louis Tunnel discharge (at DR-3A) to establish pre-injection geochemical conditions. These samples will be in addition to the depth discrete samples taken during geophysical characterization (Section 5.1.1). The samples from the Blaine Tunnel and the 517 Shaft will be obtained by U.S. EPA or their contractor personnel. Water from Silver Creek will also be sampled to characterize the carrier water prior to injection to the 517 Shaft. Baseline samples will be collected and analyzed as summarized in Table 2, in accordance with methods described in the SAP for the injection test (Appendix A of Atlantic Richfield, 2012) and governed by the QAPP in Appendix A of this Work Plan Addendum.

Water quality parameters will be measured at all baseline sampling locations. Parameters to be measured will include pH, temperature, conductivity, ORP, and DO. To measure field parameters in the 517 Shaft, a data logging sonde (In-situ Troll 9500 or similar) will be calibrated and deployed into the shaft on a cable. The sonde deployed to the 517 Shaft will measure and record pH, temperature, conductivity, and ORP; DO will be measured in grab samples from the 517 Shaft using a separate calibrated field instrument. Water quality parameters at the St. Louis Tunnel discharge (DR-3A) will be measured similarly using a calibrated data logging field instrument.

5.2 INJECTION

Injection of tracers and alkaline solutions will commence after pre-injection activities have been completed. Specific injection tasks, including assumptions, are described below. This will be the longest phase of the treatability study, with the main goals of altering water chemistry, precipitating metals, and evaluating the hydraulics of the mine workings.

5.2.1 Alkaline Solution Injection

The 2013 injection test will be a follow-on to the 2012 injection test and will implement many of the recommendations that were made based on results of the 2012 injection test (AMEC, 2013). The 2013 injection test will utilize 25% NaOH as the initial injection solution, thereby reducing consumption of injected carbonate via softening reactions (i.e., precipitation of CaCO₃). Injection of carrier water from Silver Creek is not anticipated during the start of the injection test. The injection test will start in June 2013 and will evaluate the performance of this mitigation approach for a longer duration and under different seasonal conditions, such as higher flow rates and different geochemical conditions.



Injection of an alkaline solution directly into the mine water at the 517 Shaft is expected to increase the alkalinity and pH in the 517 Shaft mine water pool and in the tunnels between the 517 Shaft and the St, Louis Tunnel discharge. The increased pH and alkalinity is expected to precipitate dissolved metals, thereby reducing discharge of metals from the St. Louis Tunnel. Field and laboratory methods will be used to monitor geochemical changes in the 517 Shaft and at DR-3A (the St. Louis Tunnel discharge). Data will be evaluated to determine treatment effectiveness and to determine changes that should be made to the injection solutions.

Initial conditions are expected to approximate baseline conditions similar to those found in early September, 2012 as summarized in Table 1, although water chemistry in early summer 2013 will not be identical. The analytical results shown in Table 1 are for samples that were taken after the Blaine Base Flow test (July 10-12, 2012), but before mine water from the Blaine Tunnel was discharged to the 517 Shaft (September 6 – 23, 2012) and before injection of alkaline solutions started on September 26, 2012. The baseline pH at DR-3A is expected to be about 6.5 su, and the initial goal is to increase the pH at DR-3A to 8.5 su by injecting 25% NaOH solution to the 517 Shaft. Although the increase in pH as a function of NaOH injection rate cannot be predicted, the initial injection rate will be about 600 mL/min based on data from titration of DR-3A samples and estimates of equilibrium water chemistry with addition of NaOH (the highest dosage of 25% NaOH that was used during the 2012 injection test was 200 mL/min). The increased pH created by NaOH injection is expected to result in absorption of atmospheric carbon dioxide (CO₂) and conversion to carbonate. The elevated pH and the conversion of CO₂ to carbonate under these conditions are expected to precipitate many metals as hydroxides or carbonates, and potentially silicates. If insufficient carbonate is provided by dissolution of atmospheric CO₂, 47% K₂CO₃ solution may be injected to the 517 Shaft along with the 25% NaOH solution.

Concentrated NaOH solution was selected because it will minimize precipitation of non-target metals such as calcium, will provide a soluble source of alkalinity, is available in bulk as a concentrated solution, and is more soluble than soda ash (Na₂CO₃) at a given temperature. Additionally, it has a low freezing point (-14 degrees Fahrenheit [°F]). Other chemicals were considered for supplying alkalinity and increasing pH, including Na₂CO₃, sodium bicarbonate (NaHCO₃), and potassium carbonate. However, these chemicals were not selected due to relatively high freezing points, handling equipment requirements, health and safety considerations, inability to sufficiently increase pH, and the probable loss of carbonate to softening reactions. Direct injection of CO₂ to the 517 Shaft was not considered because it will lower the pH, counteracting injection of NaOH.



Sodium in the injected NaOH will be monitored as a continuously injected tracer. The initial NaOH injection rate will be maintained until the sodium concentration at DR-3A achieves equilibrium (discussed further in the following section), and changes to the dosing rate and injected chemicals will be based upon observed geochemical changes at the discharge of the St. Louis Tunnel. The following decisions could be made, based on analytical and field monitoring results:

- If pH at DR-3A is below 8.5 su and/or metals concentrations at DR-3A have not decreased substantially, the NaOH injection rate may be increased.
- If the pH is above 8.5 su and/or metals concentrations have decreased substantially, the injection rate may be decreased. The pH at DR-3A will be increased no higher than 9.0 su.
- If carbonate alkalinity does not increase, or if metals that precipitate as carbonates show no decreasing concentration trend, K₂CO₃ may be injected along with NaOH. The main indicator metal for this assessment will be zinc. A concentrated K₂CO₃ solution (47% K₂CO₃ by weight) will be delivered to the site if needed as a supplemental carbonate source.

Similar conditions (equilibrium sodium concentrations at DR-3A) and decision logic will apply after any dosing rate changes have been made to the 517 Shaft.

The injection system (Figure 4) will be configured to be flexible and adaptable, with three different injection pumps with independent discharge lines. Two of the injection lines will be for chemical dosing, while the third may be used for injection of water from Silver Creek, if carrier water is needed. The chemical feed lines will use peristaltic chemical injection pumps to draw solutions from chemical storage tanks and inject these solutions to the 517 Shaft. The chemical injection pumps have been selected based on the anticipated range of alkaline solution injection and the chemical compatibility with the solutions. All system components that will handle injection chemicals will be constructed of materials that are compatible with the injection solutions. All wetted system components will be placed in secondary containment to mitigate the potential for a chemical release to the soil or Silver Creek.

Discharge lines from each chemical injection pump will pass through a totalizing flow meter for tracking injected volumes. The injection lines will extend into the 517 Shaft Access Tunnel and down the 517 Shaft. The section of each injection line that is between the flow meter and the 517 Tunnel Access portal will be placed in secondary containment. The discharge end of each injection hose will be an injection nozzle that will be placed approximately 5 feet below the surface of the 517 Shaft mine water pool to disperse and promote subsurface mixing of the injected solution and prevent the dense solutions from sinking in the 517 Shaft. If, however,



during the pre-characterization evaluation, the inflow of water to the 517 Shaft is determined to be from above the mine water pool surface, then the injection nozzle may be placed at or above the water surface.

The third injection pump will be a submersible pump placed in Silver Creek to deliver water from Silver Creek to the 517 Shaft, if it is determined that carrier water is needed to enhance flow out of the 517 Shaft. The discharge line for this pump will be a 2-inch PVC line that discharges at the collar of the 517 Shaft; injected carrier water will free fall approximately 460 feet to the mine water pool. If this carrier water system is needed, it is most likely to be used during the latter portion of the injection test, when late summer/early fall flows through the system are reduced.

The primary data set that will indicate treatment effectiveness will be changes in water chemistry at the St. Louis Tunnel discharge. Water samples from DR-3A (the St. Louis Tunnel discharge location) will be taken periodically and analyzed for total and dissolved metals concentrations; alkalinity; sulfate; and tracers. Water quality parameters (pH, temperature, conductivity, DO, ORP) will also be continuously monitored at DR-3A during the injection test. Samples will be collected and analyzed as summarized in Table 2, in accordance with methods described in the SAP for the injection test (Appendix A of Atlantic Richfield, 2012) and the QAPP included as Appendix A of this Work Plan Addendum.

Water quality parameters will be continuously monitored during the injection phase. A data logging sonde (In-situ Troll 9500 or similar) will be calibrated and deployed into the 517 Shaft on a cable before injections start. The sonde will remain deployed to measure and record pH, temperature, conductivity, and ORP. Data will be periodically downloaded from the device for evaluation. The sonde will be removed from the shaft for routine maintenance and recalibration, and then re-deployed when in-tunnel support personnel are available (at intervals of approximately two weeks).

Water samples will be obtained from the 517 Shaft to monitor geochemical changes near the injection point. Samples will be obtained using a Bennett submersible pump or a bailer (which will require in-tunnel support personnel from U.S. EPA or their contractors). Data collection activities are described further in Section 7, and the proposed sample frequency, sampling methods, and analyses are outlined in Table 2.

5.2.2 Continuous Tracer Injection

To further assess the hydraulic characteristics of the mine workings between the 517 Shaft and the St. Louis Tunnel discharge, as well as contributions from other workings, a



conservative tracer will be continuously injected at the 517 Shaft with the alkaline solution. The 2013 injection test will utilize the sodium ion in the injected NaOH as the continuously injected conservative tracer ion to verify the hydraulic connection and to estimate the mean hydraulic residence time under conditions of the test. The use of sodium as a continuously injected tracer assumes that sodium is completely conservative, that it is completely soluble in the mine water, does not adsorb significantly, and that it mixes completely into the mine water at the 517 Shaft. Further, it is assumed that sodium will not affect flow of mine water and will not react or be retarded within the mine. After mixing into the mine water at the 517 Shaft, the tracer will travel at the velocity of the water and will be measurable in samples collected from the St. Louis Tunnel discharge. The goal of continuous injection of a conservative tracer is to achieve a steady state effluent tracer concentration at the St. Louis Tunnel discharge.

An increase in sodium concentrations above pre-injection levels at DR-3A will confirm the hydraulic connection between the 517 Shaft and DR-3A. Once a steady state concentration of sodium at DR-3A is achieved, the mine water flow rate through the 517 Shaft into the St. Louis Tunnel and the mine water flow rate from the NW Cross-cut into the St. Louis Tunnel can be estimated.

Equilibrium sodium concentrations at DR-3A will also be used as part of the decision-making process for altering NaOH dosing rates. During the 2012 injection test, NaOH was not injected long enough for sodium concentrations to reach equilibrium at DR-3A. However, the 2013 injection test will be conducted for a longer duration and with higher NaOH dosing rates with the goal of achieving equilibrium sodium concentrations at DR-3A. The expected equilibrium sodium concentrations can be calculated using a simple mass balance on sodium:

$$Q_{inj}C_{inj}=Q_{out}C_{out}$$

where Q_{inj} is the injection flow rate (volume per time); C_{inj} is the injected sodium concentration (mg/L); Q_{out} is the flow rate at the St. Louis Tunnel discharge (volume per time); and C_{out} is the sodium concentration (mg/L) at the St. Louis Tunnel discharge. As an example, steady state injection of 0.5 gallons per minute (gpm) of 25% NaOH (equivalent to an NaOH concentration of 319.2 grams per liter [g/L], or a sodium concentration of 183.54 g/L) would be expected to result in a steady state sodium concentration of about 0.23 g/L at DR-3A, when the DR-3A flow rate is 800 gpm. This calculation assumes that sodium contributions from other portions of the mine workings are insignificant compared to the sodium contribution of the injected NaOH and can thus be neglected.



The initial injection rate of 25% NaOH is currently targeted as 600 mL/min to increase the pH to 8.5 su at DR-3A, assuming a flow rate of 1,000 gpm at DR-3A. The initial dosing rate will be maintained until equilibrium sodium concentrations are achieved at DR-3A. When the sodium concentration equilibrates at DR-3A, the system will approximate steady state conditions, and further decisions can be made with respect to modifying the NaOH dosage. Decision criteria and potential modifications to alkaline solution injections are described in the previous section.

The same conditions (equilibrium sodium concentrations at DR-3A) and decision logic will apply after any changes have been made to the dosing rate at the 517 Shaft. Decisions to modify the NaOH dosing rate and to add K₂CO₃ will be made in consultation with the Rico project team members.

5.2.3 Short-Term Tracer Injections

Rapid tracer injections (i.e., pulse injections) are typically used to estimate the residence time distribution of fluid in a chemical "reactor." Measurement of effluent tracer concentration over time yields information about the mean residence time of fluid in the reactor, or in this case the underground workings. In the context of the 2013 injection test, the primary goal of short-term tracer injections will be to estimate the residence time distribution for fluid traveling between the 517 Shaft injection locations and the St. Louis Tunnel discharge location. The short-term tracer injection will also confirm that mine water is flowing through the 517 Shaft to the St. Louis Tunnel discharge. This information will be useful in estimating the minimum amount of time needed for observable geochemical changes to appear in the St. Louis Tunnel discharge and also has implications for the design of future injection tests and more permanent mitigation methods within the mine workings.

Up to three short-term tracer injections will be performed during the 2013 injection test. The initial short-term tracer test will be conducted shortly after elevated sodium concentrations are observed at DR-3A in response to NaOH injections; the elevated sodium concentrations will be used to confirm a hydraulic connection between the 517 Shaft and DR-3A and will be used to estimate flows through the system. This timing will also allow longer monitoring of tracers at DR-3A to improve mass balance recovery calculations.

Additional tracer tests (using different tracer materials, so that results of the different tests are distinguishable) may be conducted later during the summer and/or fall field season as flows through the system change. Flows exiting the St. Louis Tunnel are expected to peak in June or July and decrease through the remainder of the Injection test. Pulse tracer tests will be used to quantify the residence time distribution (RTD) for the system, which can be used to calculate the mean hydraulic residence time (HRT) and to evaluate the degree of dispersion,



short-circuiting, and storage within the system. Results from different pulse tracer tests can be used to evaluate seasonal changes in the hydraulic characteristics of the mine workings.

Tracers that will be used for pulse injection during the 2013 injection test will be water soluble, conservative materials that will not react or be retarded within the mine. Tracers must also not be affected by the high pH conditions that will be present as NaOH is being injected. Sodium bromide (NaBr) and lithium chloride (LiCl) were used as tracers during the 2012 injection test and are proposed for 2013 pulse injection tracer tests. Lithium fluoride or sodium fluoride may also be considered. Organic dyes such as rhodamine and fluorescein may also be considered. Potassium salts will not be considered because potassium was found to be non-conservative when NaOH was being injected with K₂CO₃ during the 2012 injection test. Although sodium salts may be used, sodium will not be used as the primary tracer ion for short-term tracer testing because it will be continuously injected as NaOH, and pulse injection of a sodium salt is not expected to appreciably increase sodium concentrations at DR-3A.

Lithium chloride from FMC Lithium will be used for the first short-term tracer injection. LiCl was selected because background lithium concentrations are low, the analytical method for lithium is very sensitive, the material is readily available, and the material is highly soluble in water. LiCl was used as a continuously injected tracer during the 2012 injection test.

Batches of tracer solutions will be prepared by dissolving a known mass of tracer material into a known volume of water from Silver Creek. LiCl will be obtained from FMC Lithium. The target LiCl concentration will be about half of the solubility of the salt (about 550 g/L at 20 degrees Celsius [°C]). If NaBr is used, it will be obtained from Leslie's Pool Supply and prepared at a solution concentration below its aqueous solubility of about 905 g/L at 20°C. If NaBr is used, the bromide ion will be used as the tracer, rather than the sodium, to distinguish this tracer from sodium in the injected NaOH. Because dissolution of many salts is an exothermic reaction, rapid addition of salt to Silver Creek water will be avoided to prevent excessive solution temperatures. The actual concentrations of pulse tracer solutions will be determined after flow rates through the 517 Shaft and the SE Cross-cut have been estimated based on analysis of the initial continuous tracer (sodium) breakthrough at DR-3A.

The tracer solution will be rapidly injected to the 517 Shaft using one of the three injection pumps. The starting time, ending time, and flow rate will be recorded. Injection of the tracer solution will be followed by injection of Silver Creek water to ensure all tracer is injected to the 517 Shaft. If the K₂CO₃ injection pump is not in use, it may be used because this injection line will allow placement of the tracer directly into the 517 Shaft mine water pool. The Silver Creek carrier water pump and discharge line could also be used, although this system is not



preferred because the discharge point is expected to be at the top of the 517 Shaft, which may result in some loss of tracer during free fall to the mine water pool.

Tracer concentrations will be monitored at DR-3A using ion-specific electrodes (ISE) and laboratory analysis of water samples. If organic dyes are used as tracers, field instrumentation will be used to continuously monitor concentrations of these tracers at DR-3A. Tracer concentrations will be used to estimate travel time between the 517 Shaft and DR-3A and to calculate the RTD for the system, which can be used to derive the mean HRT of transport between the 517 Shaft and DR-3A. The RTD curve may also indicate the degree of dispersion, short-circuiting, and storage that occurs during transport between the injection and discharge points. Data will also be used to calculate the fraction of tracer mass that exits the system by numerical integration of the effluent concentration curves. The degree of mass recovery will yield information about the flow and transport characteristics of the system, as well as the fate of the injected tracer materials. If multiple pulse tracer tests are conducted throughout the field season, data will be used to evaluate seasonal variations in the hydraulic characteristics of the system.

Short-term tracer test data from will be evaluated to determine the hydraulic characteristics of the mine using the methods described by Kilpatrick and Cobb (1985), Levenspiel (1999), Metcalf and Eddy (2003), and Fogler (2005). Short-term tracer test results will also be compared to results of the previous pulse tracer tests (URS, 2012; AMEC, 2013).

5.3 POST-INJECTION

After injections are complete, additional post-injection monitoring will be conducted prior to demobilization from the site.

5.3.1 Post-injection Monitoring

Post-injection monitoring will be conducted for up to one month to evaluate the return to baseline geochemical conditions. The post-injection sampling and analysis program is outlined in Table 2 and will be conducted in accordance with the injection test SAP (Appendix A of Atlantic Richfield, 2012) and the task-specific QAPP included as Appendix A of this Work Plan Addendum. Post-injection sampling and monitoring will be completed at two locations for up to one month following the completion of injections:

 At the St. Louis Tunnel discharge (DR-3A), one water sample per day will be collected and shipped to laboratory for analysis. Initial laboratory analysis will consist of one sample per week, with remaining samples kept on hold for later analysis to fill data gaps. Additionally, water quality parameters will be continuously monitored at DR-3A for up to one month after completing injections.

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At the 517 Shaft, one water sample per week will be obtained from the mine water
pool in the 517 Shaft using the Bennett submersible pump or a bailer, with in-tunnel
support from U.S. EPA or their contractors. The actual number of post-injection
samples from the 517 Shaft will depend on the sampling method and the availability
of in-mine personnel for sample collection. Water quality parameters will be
continuously monitored in the 517 Shaft using the submerged water quality sonde
for up to one month after completing injections.

All post-injection samples and field data will be collected in accordance with the SAP included as Appendix A of AMEC (2012) and the task-specific QAPP included as Appendix A of this Work Plan Addendum.

5.3.2 Demobilization

Upon completion of the injection activities at the 517 Shaft and sampling activities at the St. Louis Tunnel discharge, all equipment will be decontaminated and disassembled in accordance with approved procedures. Equipment and materials will be demobilized, properly cleaned as appropriate, and stored for possible future use at the site, and equipment rentals will be returned as required. The site location will be returned to match original conditions to the extent practicable.

6.0 IMPLEMENTATION SCHEDULE

All work described in this Work Plan Addendum will be initiated and completed pending coordination and availability of Atlantic Richfield and U.S. EPA and their contractor personnel. The anticipated general schedule for the 2013 injection test is as follows:

- Phase 1, Pre-Injection:
 - o Week of April 29: Initial 517 Shaft reconnaissance
 - Week of May 13: Geophysical survey of 517 Shaft
 - June 3 June 20: system construction, startup, and commissioning; pre-injection sampling
- Phase 2, Injection: estimated duration of three months, from approximately
 June 20 through September 20, 2013. Note that the injection duration could be
 modified (reduced or increased) based on observed results and the ability to safely
 conduct work at the site (governed by weather conditions). Additionally, the
 injection start date may be modified depending on progress of pre-injection tasks
- Phase 3, Post-Injection: duration of 1 month, from late September to late October, 2013

A more detailed schedule will be developed following approval of this Work Plan Addendum. Implementation of the treatability study activities and demobilization of all equipment is



anticipated to be complete by October, 2013. These dates are subject to change depending on weather limitations and the availability of in-tunnel support personnel.

7.0 DATA COLLECTION

The field work described in this Work Plan Addendum will include water sampling and analysis and field monitoring of water quality parameters. Data collected will be reduced and evaluated to determine the effectiveness of alkaline injections at the 517 Shaft and the hydraulic characteristics of the mine workings between the 517 Shaft and the St. Louis Tunnel discharge.

Sample and data collection will be governed by the task-specific QAPP, included as Appendix A of this Work Plan Addendum. The task-specific QAPP provides guidance for field and laboratory activities, data collection activities, and sample analysis activities so that the data will meet the objectives of the treatability study. The QAPP also includes the SOPs that establish the procedures, equipment, and documentation that will be used during the treatability study field sampling and measurement activities. The Field Sampling Plan (Section 3 of Appendix A in Atlantic Richfield, 2012) describes the sampling locations, field activities, field measurements, and off-site laboratory analyses that will be used during the 2013 injection test.

8.0 REPORTING

Injection test results will be communicated via two mechanisms: (1) regular communications with the Rico project team via teleconference and/or emails during the field test; and (2) preparation of a Completion Report detailing the implementation and results of the 2013 injection test.

During the 2013 field test, regular conference calls will be conducted with the Rico project team to discuss implementation issues, status of testing, and interim results. Additional calls may be conducted, as necessary, to keep the project team informed of progress and to work through implementation issues that may arise. Key personnel from Atlantic Richfield, and U.S. EPA, as well as their contractor personnel, will be invited to participate in these calls.

After the conclusion of the field study and finalization of all data, a Completion Report will be prepared and submitted to the U.S. EPA. The report will include a comprehensive description of the treatability study and tracer tests, including a description of the methodology, any deviations from this Work Plan Addendum, results of all field monitoring and analytical data, and an interpretation of results. Data collected will be evaluated to determine the



effectiveness of alkaline injections to the 517 Shaft and the hydraulic characteristics of the mine workings. Additionally, 2013 results will be compared to previous test results, i.e., tracer test results from 2011 (URS, 2012) and 2012 (AMEC, 2013) and injection testing conducted in 2012 (AMEC, 2013). Available data from testing at the Site will be used to evaluate the hydraulics of the mine workings and the treatability of mine water at the site.

Recommendations for future actions will be presented and implications for scale-up will be discussed. The Completion Report will be a key milestone in evaluating methods for mitigating metals in the mine water that discharges from the St. Louis Tunnel.

9.0 REFERENCES

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TABLES



TABLE 1 ANALYTICAL AND FIELD MONITORING RESULTS, 2012 BASELINE SAMPLES

Rico Argentine Mine Site Dolores County, Colorado

Sample: 517 Shaft, 455 feet DR-3 sample								
	Sample: Date:	· ·	DR-3 sample 9/5/2012 17:55					
Parameter	Units	Result	Result					
Metals	Office	Result	Nesuit					
Aluminum, Total	µg/L	2,780	200					
Aluminum, Dissolved	µg/L	1,960	4.0					
Antimony, Total	μg/L	<0.50	<0.50					
Antimony, Dissolved	µg/L	<0.50	<0.50					
Arsenic, Total	μg/L	0.95	<0.50					
Arsenic, Dissolved	μg/L	<0.50	<0.50					
Barium, Total	μg/L	22.2	19.8					
Barium, Dissolved	μg/L	20.4	19.5					
Beryllium, Total	μg/L	0.84	0.54					
Beryllium, Dissolved	μg/L	0.67	0.27					
Cadmium, Total	μg/L	83.6	20.4					
Cadmium, Dissolved	μg/L	84,3	19.5					
Calcium, Total	μg/L	327,000	251,000					
Calcium, Dissolved	μg/L	336,000	247,000					
Chromium, Total	μg/L	1.3	<0.50					
Chromium, Dissolved	μg/L	<0.50	<0.50					
Cobalt, Total	μg/L	7.2	3					
Cobalt, Dissolved	μg/L	7.1	2.9					
Copper, Total	μg/L	344	37.2					
Copper, Dissolved	μg/L	248	2.5					
Hardness, Total	μg/L	943,000	710,000					
Iron, Total	μg/L	5,300	3,350					
Iron, Dissolved	μg/L	648	349					
Lead, Total	μg/L	24.8	1.5					
Lead, Dissolved	μg/L	1.6	<0.1					
Lithium, Total	μg/L	30.6	26					
Lithium, Dissolved	μg/L	31.2	26.8					
Magnesium, Total	μg/L	30,800	20,100					
Magnesium, Dissolved	μg/L	32,200	20,300					
Manganese, Total	μg/L	4,810	1,970					
Manganese, Dissolved	μg/L	5,010	1,970					
Mercury	μg/L	<0.20	<0.20					
Molybdenum, Total	μg/L	5.2	14.1					
Molybdenum, Dissolved	μg/L	2.1	13.4					
Nickel, Total	μg/L	14.4	4.8					
Nickel, Dissolved	μg/L	15.6	5.2					
Potassium, Total	μg/L	1,590	1,600					
Potassium, Dissolved	μg/L	1,600	1,630					
Selenium, Total	μg/L	0.52	<0.5					
Selenium, Dissolved	µg/L	0.51	<0.5					
Silica, Total	µg/L	18,200	16,800					
Silica, Dissolved	µg/L							
Silver, Total	µg/L	<0.50	<0.50					

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TABLE 1 ANALYTICAL AND FIELD MONITORING RESULTS, 2012 BASELINE SAMPLES

Rico Argentine Mine Site Dolores County, Colorado

Dolores County, Colorado							
	Sample:	517 Shaft, 455 feet	DR-3 sample				
	Date:	9/5/2012 18:15	9/5/2012 17:55				
<u>Parameter</u>	Units	Result	Result				
Silver, Dissolved	μg/L	<0.50	<0.50				
Sodium, Total	μg/L	9,210	10,900				
Sodium, Dissolved	μg/L	9,440	11,000				
Thallium, Total	μg/L	<0.10	<0.10				
Thallium, Dissolved	μg/L	<0.10	<0.10				
Vanadium, Total	μg/L	0.34	<0.10				
Vanadium, Dissolved	μg/L	<0.10	<0.10				
Zinc, Total	μg/L	15,200	4,080				
Zinc, Dissolved	μg/L	15,900	3,890				
General Water Chemistry and	Anions						
Alkalinity,Bicarbonate	mg/L as CaCO ₃	23.7	97.4				
Alkalinity, Carbonate	mg/L as CaCO ₃	<20.0	<20.0				
Alkalinity, Hydroxide	mg/L as CaCO ₃	 .	-				
Alkalinity, Total	mg/L as CaCO ₃	23.7	97.4				
TDS	mg/L	1,460	1,040				
TSS	mg/L	11	<5.0				
Sulfide, Total	mg/L	<0.05	<0.05				
Bromide	mg/L	<1.0	<1.0				
Chloride	mg/L	<1.0	<1.0				
Fluoride	mg/L	3.1	2.2				
Sulfate	mg/L	506	622				
Nitrogen, Nitrate	mg/L		<0.10				
TOC	mg/L	1.4	<1.0				
Field Monitoring Parameters*							
рН	s.u.	6.12	6.92				
Temperature	°C	19.3	18.41				
Conductivity	μS/cm	1,734	1,332				
Dissolved Oxygen	mg/L	4.15	2.58				
ORP	mV	77.1	95				

Notes/Abbreviations

- -- = Not analyzed
- * = All field monitoring parameters were provided by Anderson Engineering Company.

°C = degrees Celsius

μg/L = micrograms per liter

μS/cm = microSiemens per centimeter

CaCO₃ = calcium carbonate

mg/L = milligrams per liter

mV = millivolts

ORP = oxidation reduction potential



TABLE 2 SUMMARY OF SAMPLING AND ANALYSIS PROGRAM, 2013 INJECTION TEST

Rico-Argentine Mine Site Dolores County, Colorado

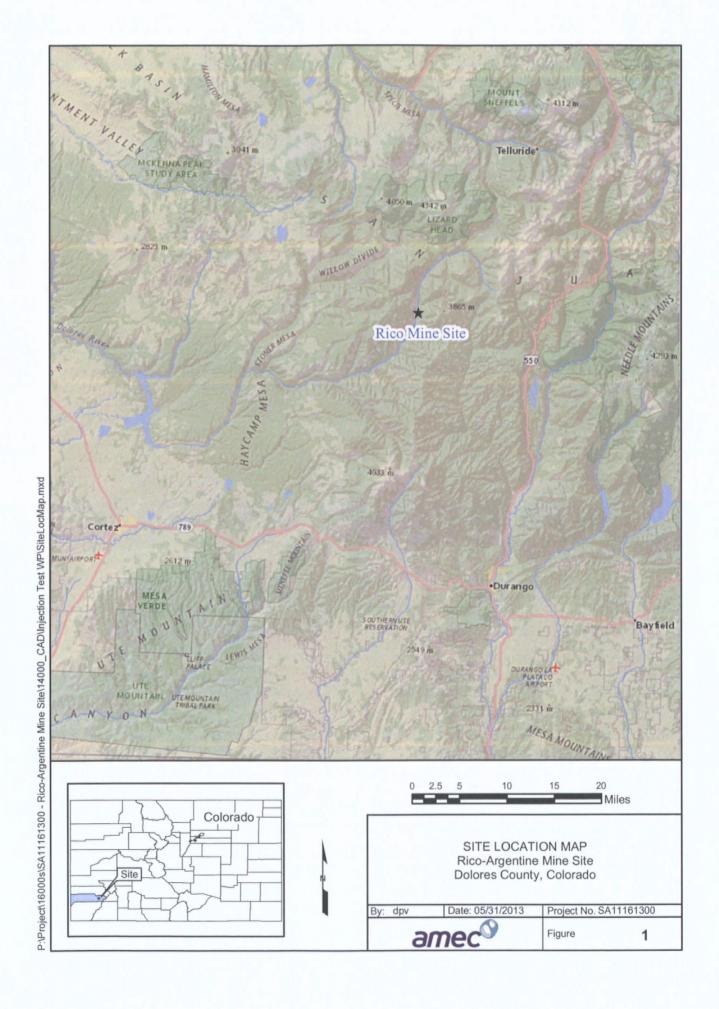
Phase	Location	Estimated Duration	Sample Frequency	Estimated Number of Samples	Sampling Method	Analyses	Rationale
Geophysical Characterization	517 Shaft - multiple depth discrete samples*	-	1 depth-discrete sample	5*	Bennett submersible pump	Field Measurements (1); Lab (3); Lab (4)	Baseline conditions as a function of depth within the shaft; used with other information to determine flows into and out of the shaft
	517 Shaft Injection Zone	_	1 sample	1	Bennett submersible pump or bailer	Field Measurements (1); Lab (3); Lab (4)	Baseline conditions at injection point
Baseline/ Pre-Injection	Silver Creek	-	1 sample**	1	Grab	Field Measurements (1); Lab (3); Lab (4)	Characterize carrier/dilution water; sample to be taken prior to use
-	St. Louis discharge DR-3A	_	1 sample	1	Grab or Autosampler	Field Measurements (1); Lab (3); Lab (4)	Baseline conditions at St. Louis discharge point
	517 Shaft Injection Zone	1 month***	1 sample every 2 weeks†	4 .	Bennett submersible pump or bailer	Field Measurements (1); Lab (3); Lab (4)	Monitor geochemical changes at 517 Shaft injection point
Each Injection Step	St. Louis discharge DR-3A	1 month***	1 sample per day (5)	30	Grab or Autosampler	Field Measurements (1); Field Analytical (2); Lab (3); Lab (4)	Evaluate geochemical effects of injections & tracer test results
	DR-3A	1 month***	2 samples per day (5)	60 (a)	Autosampler	Lab (4)	Monitor tracer study constituents, if needed
	517 Shaft Injection Zone	1 month***	1 sample per week†	4	Bennett submersible pump or bailer	Field Measurements (1); Field Analytical (2); Lab (3); Lab (4)	Monitor geochemical changes at 517 Shaft injection point and return to baseline conditions
Post-Injection	St. Louis discharge	~ I 1 month I	1 sample per week	4	Grab or Autosampler	Field Measurements (1); Field Analytical (2); Lab (3); Lab (4)	Evaluate residual effects of injections and return to baseline conditions
	DR-3A		1 sample per day (5)	30 (a)	Autosampler	Lab (4)	Monitor tracer study constituents, if needed

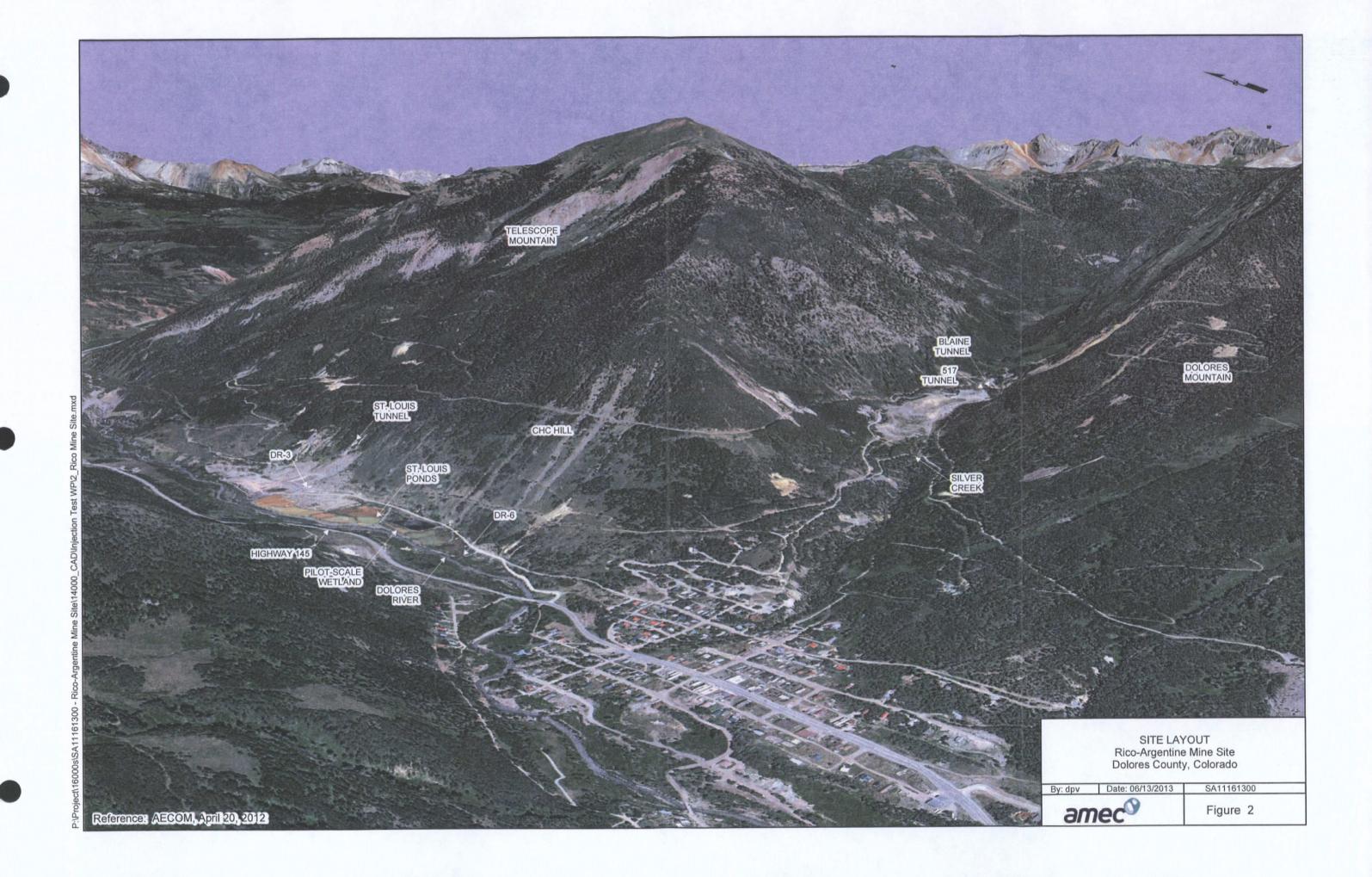
Notes/Abbreviations:

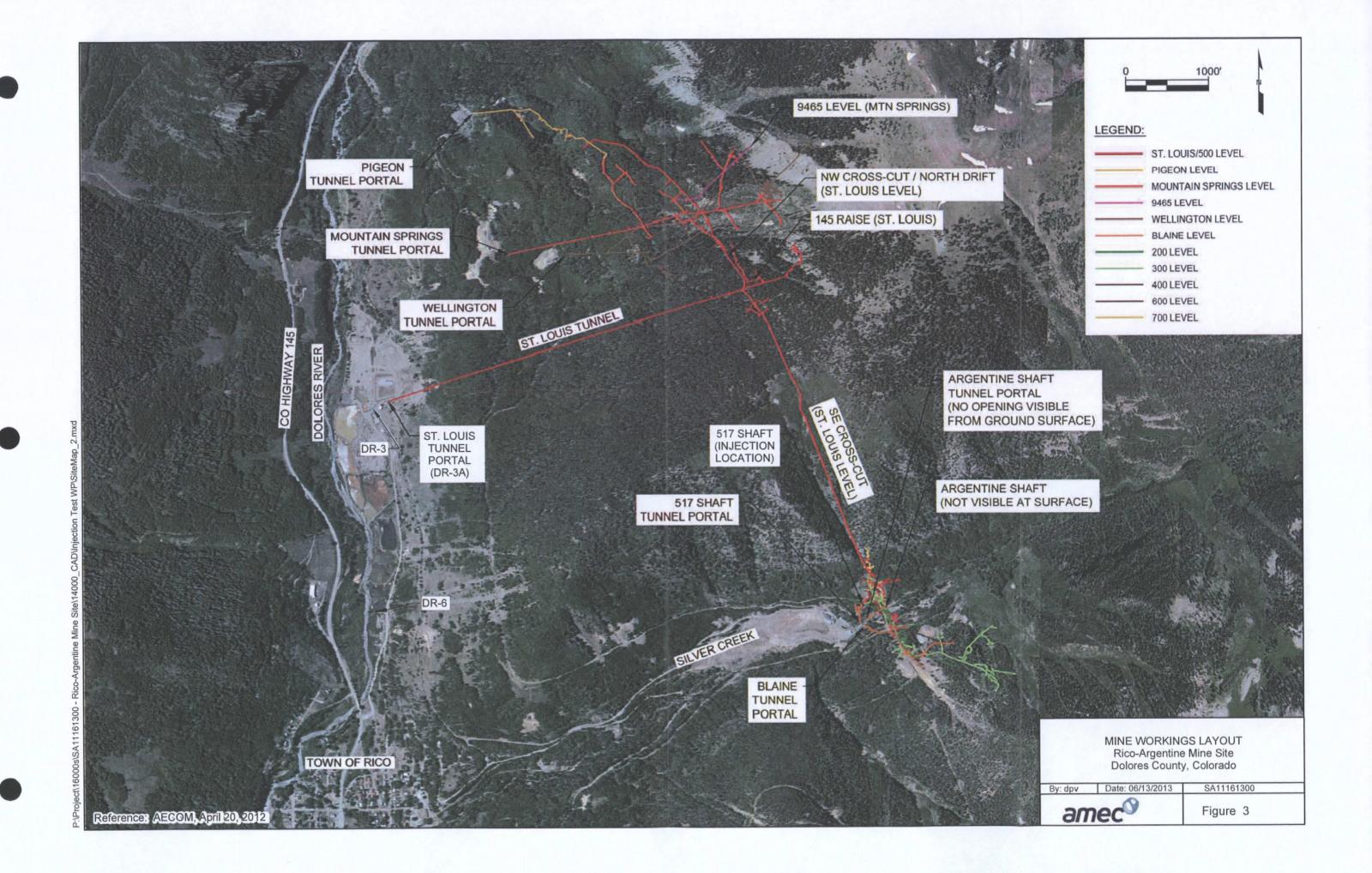
- *- number of samples to be taken to be determined based on in-field water quality measurements and geophysical observations in the 517 Shaft; number is an initial estimate.
- ** Sample of Silver Creek water will only be taken if this water is used as carrier water or dilution water.
- *** duration of each injection step assumed to be 1 month; this may be modified based on actual results of alkaline solution injections and tracer testing.
- † The goal is to obtain one sample every 2 weeks from 517 Shaft injection zone; the actual number of samples will be dependent on sampling method. If bailer is required, the actual number of samples will depend on availability of in-mine personnel (U.S. EPÄ, CDRMS, and/or their contractors) to collect samples from the 517 Shaft, accessibility, weather conditions, etc.
- (1) Typical field measurements consist of pH, temperature, specific electrical conductivity, ORP, and DO using calibrated instrumentation.
- (2) Field analytical consists of ion-specific electrode measurement of tracer ions (when applicable, to monitor pulse tracer injection output only), and/or photometer measurement of alkalinity.
- (3) Lab Analyses: total and dissolved metals; alkalinity; and sulfate using methods shown in Table A-1 in Appendix A.
- (4) Lab Analyses (tracers): chloride, bromide, fluoride, lithium, sodium, and/or potassium using methods shown in Table A-1 in Appendix A; specific tracer ions to be analyzed dependent on what tracers are used.
- (5) Sample frequency and/or analyte list may be reduced, based on evaluation of tracer results and system response to alkaline solution injection.
- (a) Lab will be directed to place these extra daily samples on hold. AMEC will provide direction to lab on additional samples to analyze, based on initial sample results.

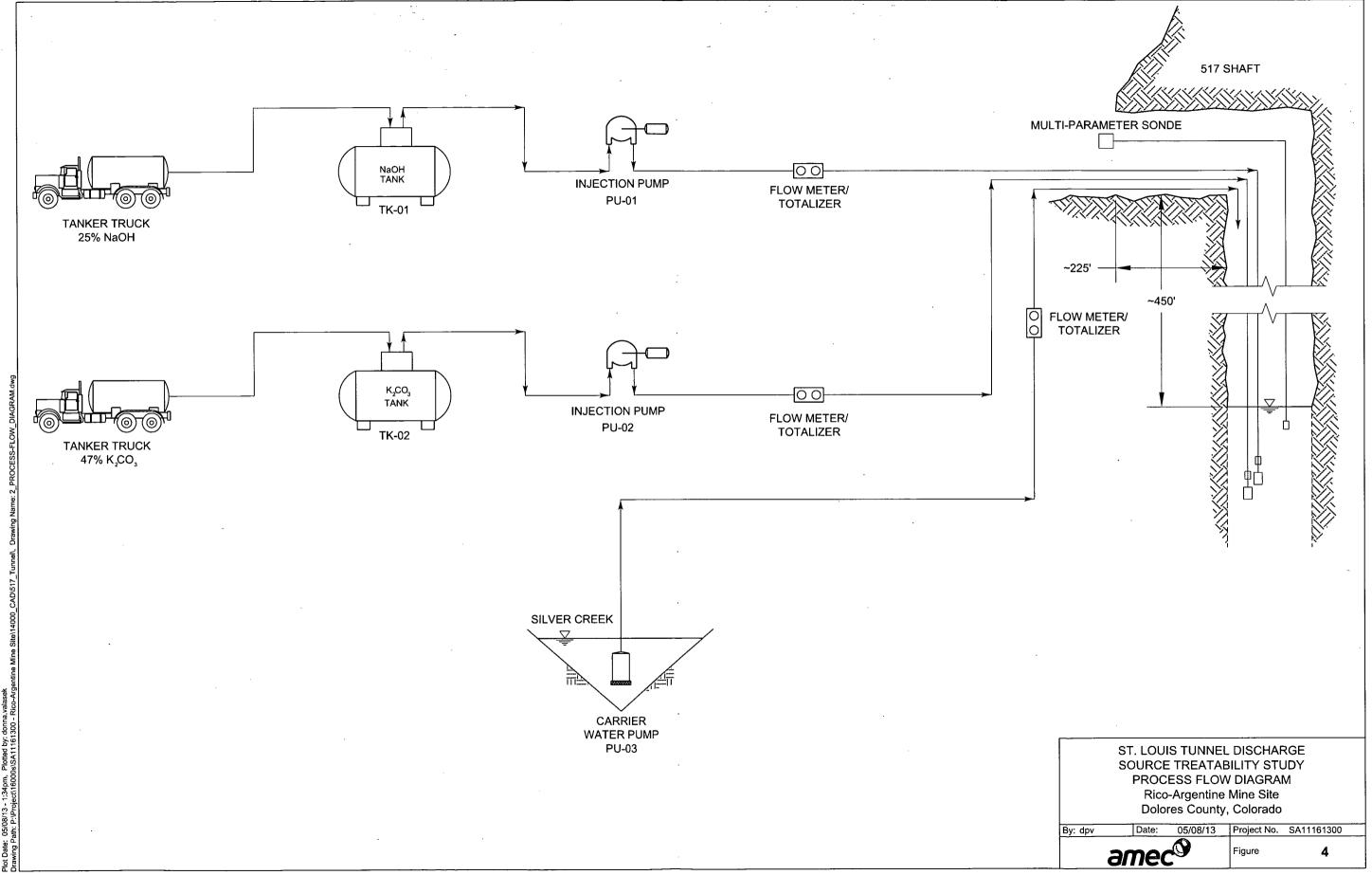


FIGURES











APPENDIX A

St. Louis Tunnel Discharge Source Mine Water Treatability Study Quality Assurance Project Plan



APPENDIX A ST. LOUIS TUNNEL DISCHARGE SOURCE MINE WATER TREATABILITY STUDY QUALITY ASSURANCE PROJECT PLAN

Rico-Argentine Mine Site – Rico Tunnels Operable Unit OU01 Dolores County, Colorado

Prepared for:
Atlantic Richfield
La Palma, California

Prepared by:

AMEC Environment & Infrastructure, Inc.
Rancho Cordova, California

June 2013 (Rev 0)

Project No. SA11161313



This Quality Assurance Project Plan has been reviewed and approved by the applicable authority representing the project team. In addition, by signature below, we certify that all personnel working on the project have been trained to this plan:

Approvals:

Marc Lombardi, CEM, PG

Now R Saulati

AMEC Project Manager

Lynda Lombardi

AMEC QA Manager



TABLE OF CONTENTS

		Page				
1.0	QUALITY ASSURANCE PROJECT PLAN	A-1				
2.0	PROJECT ORGANIZATION					
3.0	PURPOSE AND OBJECTIVES					
4.0	EVALUATION OF TREATMENT OBJECTIVES 4.1 SAMPLING LOCATIONS 4.2 SAMPLE TYPES 4.3 HEALTH AND SAFETY PLAN	A-4 A-5				
5.0	FIELD OPERATION PROCEDURES 5.1 STANDARD OPERATING PROCEDURES 5.2 COLLECTION OF REPRESENTATIVE SAMPLES 5.3 SAMPLE LABELING 5.4 SAMPLE HANDLING, CUSTODY AND TRANSPORT 5.5 SPECIAL TRAINING	A-6 A-7 A-7				
6.0	ANALYTICAL PROCEDURES	A-9				
7.0	QA/QC OBJECTIVES	A-10 A-11				
8,0	CORRECTIVE MEASURES	A-11				
9.0	DOCUMENTS AND RECORDS					
10.0	REFERENCES	A-13				
	TABLES					
Table	A-1 Methods, Holding Times, and Preservation Requirements					
	FIGURES					
Figure	e A-1 Organization Chart					
	ATTACHMENTS					
Attacl	hment A-1 Standard Operating Procedures					



APPENDIX A ST. LOUIS TUNNEL DISCHARGE SOURCE MINE WATER TREATABILITY STUDY QUALITY ASSURANCE PROJECT PLAN

Rico-Argentine Mine Site – Rico Tunnels Operable Unit OU01 Dolores County, Colorado

1.0 QUALITY ASSURANCE PROJECT PLAN

Quality Assurance (QA) is a system of activities, the purpose of which is to provide assurance that defined standards of quality are met with a stated level of confidence. A QA program is a means of integrating the quality planning, quality assessment, quality control (QC), and quality improvement efforts to meet user requirements. Included are all actions taken by project personnel, and the documentation of laboratory and field performance. Project-specific QA/QC requirements developed based on the planned data objectives are specified in this Quality Assurance Project Plan (QAPP). The objective of the quality assurance program is to reduce measurement errors and to produce results of acceptable and known quality. The QAPP specifies the necessary guidelines to ensure that the measurement systems remain in control and provides detailed information on the analytical approach to ensure that data of acceptable quality is obtained to achieve project objectives.

Since we are only temporarily changing the mine water quality through additives that are not sustainable and do not represent the true character of the surface water or groundwater, this QAPP considers the more directed and logical planning process for short-term environmental data collection activities associated with source mine water treatability studies and treatment option evaluations through finite treatability and/or testing. Such short term data collection programs are designed to properly collect and evaluate screening and/or definitive data in a limited amount of time without the constraints of a rigorous QA/QC program. The environmental data generated through implementation of the associated treatability and/or bench scale testing will serve to provide information to make further decisions regarding a long-term response and provide additional data and information to support the design of a sustainable, full-scale treatment system for source mine waters discharging from the site into state rivers. Continued monitoring of surface water and groundwater that provide additional data and information to support monitoring goals and are addressed in a separate, long-term, strategic QAPP (Atlantic Richfield, 2013) which follows the more rigorous guidance document (U.S. EPA, 2006), as required by the Unilateral Administrative Order (UAO) for Removal



Action issued by the U.S. EPA Region 8 (U.S. EPA) for the Rico-Argentine Mine Site (U.S. EPA, 2011b).

This Source Mine Water Treatability Study QAPP will guide the collection and management of data to be used to complete an evaluation of alkaline chemical treatment in the 517 Shaft for the removal of metals prior to the mine water discharging from the St. Louis Tunnel Adit and ultimately to the Dolores River as described. Such evaluations are integral in completion of Task E- Source Water Investigations and Control of the Removal Action Work Plan (U.S. EPA, 2011a). The components of any such treatability studies and/or bench scale studies will include a short-term application for remediation, assessment of remedial effectiveness, and specifications that can be used to evaluate long-term options for remediation. As such, this task-specific QAPP is intended to complement the existing Surface Water and Groundwater QAPP implemented for the site (Atlantic Richfield, 2013). The following sections provide information on the task-specific project organization, data management, use of data quality indicators, limitations on data use and a summary of the QC analyses associated with the field and laboratory measurements to be obtained during the treatability study described in this St. Louis Tunnel Discharge Source Mine Water Treatability Study Work Plan Addendum – Rico-Argentine Mine Site - Rico Tunnels, Operable Unit 1, Dolores County, Colorado (Work Plan Addendum). It will also serve as a general reference for future treatability studies or pilot testing conducted to evaluate potential water treatment technologies using appropriate levels of QA/QC.

2.0 PROJECT ORGANIZATION

The organization of the project team is shown in Figure A-1 (Organization Chart). The U.S. EPA Emergency Response Manager will provide oversight of the UAO activities specific to the investigation and control of source mine water task to be completed by the responsible party, Atlantic Richfield Company (Atlantic Richfield). As primary contractor for the treatability studies, AMEC will assist Atlantic Richfield in providing strategy and design, budget control, and the necessary resources to implement and complete the task.

2.1 DISTRIBUTION OF QAPP

Distribution of any related work plans that specify data collection in support of treatability studies and/or pilot studies designed to support the completion of Task E- Source Mine Water Investigations and Control of the Removal Action Work Plan (U.S. EPA, 2011a) will incorporate this QAPP in its entirety. Any subsequent revisions to this QAPP will be formally distributed to the parties receiving the respective work plans as directed by the U.S. EPA.



Changes or revisions to the procedures described in this QAPP will be incorporated into the respective Work Plans as appropriate for future pilot studies or treatability evaluations at the site for approval by the U.S. EPA.

3.0 PURPOSE AND OBJECTIVES

The primary purpose of any pilot testing or treatability study is to evaluate the effectiveness of the described in-situ chemical applications in achieving or approaching the water quality goals under actual and/or simulated field conditions (source water character, flow rates, weather, etc.). Testing will include the collection of data describing the characteristics of the technology, including the performance and reliability of the technology components and the level of operation requirements. The test will identify and assess environmental inputs and outputs, including chemical usage, generation of by-products or residuals, and other design requirements.

The testing objectives include verifying the reduction of metals loading in discharges from the St. Louis Tunnel Adit to the Dolores River using in-situ alkaline chemical treatment. Water quality measurements for field and laboratory, will be used to gain a better understanding for the variation of treatment performance over time. The data from the field measurements (pH, conductivity, dissolved oxygen, temperature, oxidation reduction potential, and alkalinity) will be factored in to the overall evaluation of treatment effectiveness. The removal of metals from discharge water will be verified by laboratory analyses. The desired result is to significantly reduce concentrations of cadmium, copper, lead, manganese and zinc, while not adversely increasing the concentration of other potential pollutants.

If results sufficiently show the technologies studied are effective and reliable, data generated from the treatability study may be used to design a permanent system for treating impacted waters at the site. Information from this study will provide an initial assessment of the applicability of selected technologies.

3.1 SCOPE OF WORK

As described in detail in the Work Plan Addendum, the field treatability study will include continuous injection of one or two alkaline solutions to mine water at the 517 Shaft for approximately three months. Sampling and test measurements for specific metals and water quality parameters will occur prior to the start of the test, during the injection of alkaline solution(s), and post injection. The field test includes the following phases:



- 1. Baseline sampling. Water samples and field measurements taken before any test injections will establish the initial conditions.
- Continuous sampling. An existing auto-sampler with continuous monitoring device will be employed to collect mine water samples and measure water quality parameters in place during the test injection period.
- 3. Flow rates: Flow rates will be measured using existing equipment installed at the sampling location at intervals coinciding with sample collection.
- 4. Post-injection. After injections are complete, additional water samples and field measurements will be taken. The purpose of these samples is two-fold: (1) to determine how long the effects of the alkaline injections last, and (2) improve the mass balance on tracers.

Mine water samples and water quality measurements will be obtained primarily from the 517 Shaft injection locations and the St. Louis Tunnel discharge location, although some samples of injected solutions may also be obtained. Chemical analysis of mine water samples will be conducted both in the field and at a fixed analytical laboratory. The schedule for sample collection is provided in Table 1 of the Work Plan Addendum.

4.0 EVALUATION OF TREATMENT OBJECTIVES

Analytical data and field measurements that will be collected in accordance with the Work Plan Addendum and this QAPP will be used for the following purposes:

- Evaluate the effectiveness of alkaline treatment of mine water at the 517, with respect to metals concentrations, alkalinity, and pH;
- Evaluate the hydraulic characteristics (e.g., flow rates, residence time distribution) of the Rico-Argentine mine workings between the 517 Shaft injection point and the St. Louis Tunnel Adit; and
- Monitor time vs. concentration as conditions return to "baseline" in the mine water at the 517 Shaft and in discharges from the St. Louis Tunnel Adit.

4.1 SAMPLING LOCATIONS

Water samples will be obtained and water quality parameters will be measured at two locations: (1) the 517 Shaft injection location; and, (2) the St. Louis Tunnel discharge (DR-3A). Flow measurements will also be obtained from co-located, existing equipment (DR-3). Additional grab water samples will be collected from Silver Creek if the need for carrier water is determined for use at the injection line. The sampling locations are illustrated on Figures 2 and 3 of the Work Plan Addendum.



4.2 SAMPLE TYPES

All samples to be collected during the treatability study will be mine water samples. Sample types submitted for testing purposes will include the composite samples taken from an automated sampling device, grab samples, and QC samples. Field water quality parameters will be collected by direct measurement.

Automated Samplers

Composite samples will be collected using an automated sampler installed in 2012 at the discharge stream from DR-3A (Atlantic Richfield, 2012) as shown on Figure 2 of this Work Plan Addendum. The automated sampler will be programmed to draw equal volumes of sample at the frequency given in Table 1 of the Work Plan Addendum. Samples taken in this manner will therefore be flow-proportional composite samples. Field personnel will ensure proper operation of the automated sampler in accordance with SOP 9.0.

Grab Samples

Grab samples will be collected to confirm field measurements for pH, conductivity, dissolved oxygen, temperature and oxidation reduction potential. Grab samples will also be collected from the 517 Shaft location shown on Figure 2 of this Work Plan Addendum.

Bulk grab samples may be collected to support additional chemical treatment studies requiring substantial sample volume for testing.

QC Samples

Laboratory analyses will include prepared QC samples to assess precision and accuracy at a frequency of five percent in accordance with the laboratory SOPs. Additionally, at a minimum, one composite sample will be split during field sampling activities, and the duplicate field sample will be submitted to the laboratory for the purpose of assessing QC. The field duplicate samples will not be identified to the laboratory as duplicates. Results of QC samples will be included in the laboratory analytical reports.

During any off site treatment evaluations, split samples will be collected and submitted to Pace Laboratories for confirmation testing.



Direct Measurements:

Field water quality measurements will be obtained by direct measurement of the mine water either by equipment installed on the automated sampling devices, or by deployment of hand held equipment directly into the water body.

Sample Retention

Samples not selected for initial analyses will be retained by the analytical laboratory at the required temperature for up to six months following field sampling. In the event of additional data needs or laboratory sample loss, this retained sample volume may provide additional volume for analysis.

4.3 HEALTH AND SAFETY PLAN

The Task Specific Health and Safety Plan for the site and the Pace Laboratories' safety plan are on file and can be made available upon request.

5.0 FIELD OPERATION PROCEDURES

5.1 STANDARD OPERATING PROCEDURES

AMEC has developed task specific SOPs (Attachment A-1) to describe field procedures for measuring water quality parameters and collecting samples for testing purposes. The SOPs establish the procedures, equipment, and documentation that will be used during the field sampling, data measurement, and analytical activities for the described St. Louis Tunnel discharge treatability study. These SOPs cover aspects of the treatability study related to sampling, sample handling, documentation, and field measurement methods. These SOPs will be followed during field activities to ensure that all activities are completed consistently and properly documented. The most current versions of the SOPs included in Attachment A-1 are as follows:

SOP 1.0 (rev. 1)	Field Documentation and Sample Handling
SOP 2.0 (rev. 1)	Sample Collection Techniques and Data Collection strategies
SOP 3.0 (rev. 1)	Field Measurements - Water
SOP 4.0 (rev. 1)	Equipment Decontamination



SOP 5.0 (rev. 1) Investigation Derived Waste Disposal

SOP 6.0 (rev. 1) Stream Flow Measurement and Surface Water Sampling

SOP 9.0 (rev. 1) Operation and Maintenance of Automatic Water Sampling Equipment

Revisions to SOPs are documented in the revision log included at the end of each respective document to alert the user of any recent changes in procedures, and include the date which the revised SOP was implemented.

5.2 COLLECTION OF REPRESENTATIVE SAMPLES

The sample collection techniques will be performed in strict accordance with those described in SOP 2.0, included in Attachment A-1. Examples of paperwork included in the SOP include daily field records, photo logs, and general sampling equipment necessary to conduct any type of sampling. Table A-1 identifies the required sample volumes, sample preservation methods, types of sample containers, packing and shipping requirements, documentation requirements, and holding times.

5.3 SAMPLE LABELING

The unique sample designations to be used during the treatability study are defined in this section. To maintain organization of data, sample identification numbers will include a sample location identifier. The sample date and time will be recorded and used to correlate to the phase of the study (pre-injection, injection, or post-injection). Location identifiers for samples will be as follows:

Injection Line – Location identifier is "517 Inject".

<u>517 Injection Point</u> – The location identifier for the 517 Shaft will include the depth at which samples are taken. For example, if a sample is taken from 465 feet below the shaft collar, the location identifier will be "517Shaft465".

St. Louis Tunnel Discharge -- Location identifier is "DR3A", which corresponds to the established automated surface water sampling station installed in 2012 (AMEC, 2013).

As an example, a sample taken on 21 September 2013 from the St. Louis tunnel discharge will be designated as "DRA3130921.



Sample containers will be labeled with self-adhesive labels, with all necessary information filled out using waterproof ink. At a minimum, each sample label will contain the following information:

- · project name;
- · site location;
- sample identification code;
- date and time of sample collection, with sampler's initials;
- analyses required;
- · method of preservation, if used; and
- sampler's initials.

5.4 SAMPLE HANDLING, CUSTODY AND TRANSPORT

The sample handling and analysis procedures are described SOP 1.0, included in Attachment A-1. Examples of paperwork included in the SOP include project specific chain-of-custody forms, sample logs, and sample labels. Samples will be shipped by overnight courier to the testing facility. Sample shipment will be scheduled to prevent the exceeding any required holding period.

Information on the custody, transfer, handling, and shipping of samples will be recorded by the sampling personnel on a chain of custody (COC) form provided in SOP 1.0. A COC form will be completed for each set of samples shipped together to the destination testing facility.

5.5 SPECIAL TRAINING

All personnel performing non-emergency work at the site on behalf of Atlantic Richfield will have current twenty-four, or forty-hour and eight-hour refresher Hazardous Waste Operations and Emergency Response (HAZWOPER) certification per 29 CFR 1910.120 (www.osha.gov). In addition, personnel responsible for operating mechanical equipment, including pumps, generators, and mixing equipment, will receive the necessary operating instruction on that equipment. Sampling personnel will be trained in the use of industry-standard practices and those specified in the SOPs (Attachment A-1). Sampling oversight will be provided by a qualified scientist or engineer.



U.S. EPA and/or their contractor will be utilized to provide "in-tunnel" sample collection support at the 517 Shaft as necessary. Due to accessibility at the 517 Shaft, specific training as required by the Mine Safety and Health Administration is required for field personnel entering underground mine spaces.

6.0 ANALYTICAL PROCEDURES

Samples collected for off-site laboratory testing will be sent to Pace Analytical Laboratories in Lenexa, Kansas, an accredited environmental testing laboratory through the National Environmental Laboratory Accreditation Program (Kansas NELAP Certificate No. E-101116), using proper chain of custody procedures and applicable U.S. EPA approved methodologies (U.S. EPA, 1983) presented in Table A-1. The laboratory will adhere to the additional QC requirements set forth in Atlantic Richfield's Technical Requirements for Environmental Laboratory Services (Atlantic Richfield, 2011) which provides quality standards for contracted laboratories performing work for Atlantic Richfield. Laboratory results will be provided to AMEC for data verification and evaluation of the effectiveness of the injection activities.

The specific laboratory testing to be performed on the respective treatability study samples is outlined in Table 1 of the Work Plan Addendum. The methods, units of measurement and estimated sensitivity levels for the analytes of interest are provide in Table A-1.

7.0 QA/QC OBJECTIVES

Quality assurance and quality control (QA/QC) of the equipment calibration, equipment operation, process control, measure water quality parameters and strict adherence to safety measures shall be maintained throughout the data collection program. The QA/QC objectives are in place to ensure that strict methods and procedures are followed so that the data obtained from the studies are valid for use for evaluation of treatment options. They are also designed to ensure that the conditions under with data are obtained are properly recorded and can be directly linked to the data.

The laboratory, operational, and environmental data objectives are based on requirements outlined in the Work Plan Addendum. The Work Plan Addendum outlines specific data objectives that ensure sufficient analytical measurements of contaminant removal performance in order to credibly evaluate the long-term removal performance of the technology under varying conditions.



7.1 QUALITY CONTROL INDICATORS

To assess the quality of the data generated for this treatability study, two important data quality indicators are of primary concern: (1) precision; and (2) accuracy. Precision can be defined as the degree of mutual agreement of independent measurements generated through repeated application of the process under specified conditions. Accuracy is the degree of agreement of a measured value with the true or expected value.

Precision

Precision is generally measured by laboratory/matrix spiked sample duplicates and field sample duplicates. In the case of duplicates, precision is evaluated by expressing, as a percentage, the difference between results of the sample and sample duplicate results. The relative percent difference (RPD) is calculated as:

RPD = (Maximum Value - Minimum Value) x 100(Maximum Value + Minimum Value)/2

For three or more measurements, precision is evaluated by the standard deviation of the multiple measurements relative to the mean, i.e. the relative standard deviation (RSD), according to the following equation:

$$RSD = (SD/X_{avg}) \times 100$$

where SD is the standard deviation and $\mathbf{X}_{\mathrm{avg}}$ is the average of the multiple concentrations.

Accuracy

To determine and evaluate accuracy, known quantities of select target analytes were spiked into selected field samples. Equipment used to provide data for this project was tested for accuracy through the analysis of calibration check standards and laboratory control samples. To determine matrix spike recovery, the following equation was applied:

% Recovery =
$$100 \times (C_s - C_u)/C_a$$

where C_s is the analyte concentration in spiked sample, C_u is the analyte concentration in the unspiked sample, and C_a is the analyte concentration added to sample.



7.2 EVALUATION OF FIELD MEASUREMENTS AND ANALYTICAL DATA

The data produced by the water quality and field analytical measures will be evaluated as falling within acceptable QC limits for those measures based on performing a calibration check, or measurements with a secondary device (e.g., YSI or fixed laboratory analysis) as described in SOP 3.0. Validation includes calibrations, test procedures, acceptance criteria and documentation of results.

Flow rate measurements will be evaluated for acceptance on the basis of meeting the stated objective for flow rates established in the Work Plan Addendum. The method of measuring flow rates is given in SOP 6.0.

Laboratory analytical data will be evaluated for acceptance based on the data falling within the QC limits as reported by Pace Laboratory, and outlined in the laboratory's SOP for the parameters analyzed during the treatability study.

7.3 ASSESSMENT CRITERIA

Laboratory data will be reported after it has passed QA review (data verification) by the laboratory following completion of the respective sample testing. Data acceptability will be based on the analytical results being with the acceptable criteria for accuracy and precision described in the laboratory SOPs for each analyte. These include percent recovery in spiked samples, accuracy with known standards and relative percent differences in duplicates. The completeness of the analysis will be judged by the laboratory project manager by ensuring that all of the required information has been appropriately reported. All laboratory data will be maintained in the project files.

A desktop review of all field records and field measurement data will be performed prior to finalizing the data for reporting purposes. The review will assess completeness of the documentation, acceptability of instrument calibrations and appropriate reporting of units of measure.

A relational database using Microsoft Access® software will be maintained with field and laboratory analytical measurements collected during the study.

8.0 CORRECTIVE MEASURES

Corrective actions for laboratory analyses performed are outlined in the Pace Laboratory Quality Assurance Manual. When analytical parameters fall outside of the relevant



acceptance criteria, corrective actions will be taken. Such actions may include: reanalysis of samples, reanalysis of laboratory QC samples, re-calibration of instrumentation followed by reanalysis. Corrective actions may also include measures to prevent further occurrence of the problem. Any problems with analysis will be appropriately documented in the laboratory report and communicated to the project team.

Nonconformance with field analytical measurements can include measurements which appear to be anomalous, measurements that exhibit drift of the instrumentation, or failure to provide a measurement. Corrective actions performed by field personnel can include repeating the measurement, check of calibration standard measurement, re-calibration of the instrument, or replacement of the instrument. Corrective actions taken will be noted in the field documentation according to SOP 3.0.

9.0 DOCUMENTS AND RECORDS

Sampling program records are defined as completed, legible documents, which furnish objective evidence of the quality and completeness of the data acquired pursuant to the requirements of the project activities. These records will be organized, filed and maintained under the direction the AMEC Project Manager and at a minimum will include:

- Original copies of all field sampling data sheets;
- Field copies and original (laboratory) copies of all COC forms;
- Personnel training records;
- Incoming and outgoing correspondence related to the project activity (e.g., letters, telephone conversation records, faxes, and hard copies of e-mail messages);
- · As-received laboratory reports and data packages;
- Access database for compilation of laboratory electronic deliverables and field water quality measurements;
- Assessment and/or technical review reports; and
- Final versions of work plans, field sampling plans and this QAPP.

All records will be retained for a minimum period of 10 years as required by the UAO (U.S. EPA, 2011b).



10.0 REFERENCES

- AMEC, 2013. St. Louis Tunnel Discharge Source Mine Water Treatability Study Completion Report. May, 2013.
- Atlantic Richfield, 2011. Technical Requirements for Environmental Laboratory Analytical Services, BP Laboratory Management Program (LaMP), Revision 10.1. December, 2011.
- Atlantic Richfield, 2012. St. Louis Tunnel Discharge Source Mine Water Treatability Study Work Plan. Rico-Argentine Mine Site, Dolores County, Colorado. August. (prepared by AMEC Environmental & Infrastructure, Inc.). August, 2012
- Atlantic Richfield, 2013. Quality Assurance Project Plan for Surface Water and Groundwater.
 Rico-Argentine Mine Site, Rico, Colorado. May. (prepared by Anderson Environmental Company, Inc. et al.). June, 2013
- U.S. EPA, 1983. Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79/020. March, 1983 (and subsequent amendments).
- U.S. EPA, 2006, EPA Requirements for Quality Assurance Project Plans (QA/R-5), EPA/240/B-01/003, May, 2006 (revised).
- U.S. EPA, 2011a, Removal Action Work Plan Rico-Argentine Mine Site Rico Tunnels, Operable Unit OU01 Rico, Colorado, EPA Region 8, for Atlantic Richfield Company, March 9, 2011.
- U.S. EPA, 2011b, Unilateral Administrative Order for Removal Action (UAO), Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) Docket No. 08-20011-0005, March 23, 2011.



TABLES



TABLE A-1 METHODS, HOLDING TIMES, AND PRESERVATION REQUIREMENTS SOURCE MINE WATER TREATABILITY STUDY QUALITY ASSURANCE PROJECT PLAN

Rico-Argentine Mine Site Dolores County, Colorado

Parameter	Method Reference	Container	Suggested Volume ¹	Preservation ²	Estimated Detection Limit	Maximum Holding Time	
	Laboratory Analyses						
Metals Aluminum Arsenic Cadmium Calcium Chromium Cobalt Copper Iron Lead Lithium Nickel Manganese Magnesium Mercury Potassium Selenium Silicon Sodium Zinc	EPA 200.7/ 200.8/245.1	P	500 mL	HNO₃ to pH<2; Field filtered for dissolved metals	50 ug/L 1 ug/L 0.5 ug/L 1 ug/L 1 ug/L 1 ug/L 50 ug/L 1 ug/L 1 ug/L 50 ug/L 50 ug/L 500 ug/L 500 ug/L 1 ug/L	28 days for Hg; 6 months for other metals	
Alkalinity (as CaCO₃) Bicarbonate alkalinity Carbonate alkalinity Hydroxide alkalinity	SM 2320B	Р	300 mL	None	20 mg/L 20 mg/L 20 mg/L	14 days	
Anions Bromide Chloride Fluoride Sulfate	EPA 300.0	Р	100 mL	None	1 mg/L 1 mg/L 0.5 mg/L 1 mg/L	28 days	
Field Measurements							
рН					0.1 unit	15 minutes	
Conductivity	Field SOP 3.0	Р	1,00 mL	None	0.1 µS/cm	15 minutes	
Temperature					0.1 °C	15 minutes	
Oxidation Reduction Potential					0.1 mV	15 minutes	
Dissolved Oxygen					0.2 mg/L	15 minutes	
Alkalinity	Field SOP 3.0	Р	50 mL	Field filtered	25 mg/L	24 hours	
Tracer Anions ³	Field SOP 3.0	Р	50 mL	Field filtered	5 mg/L	28 days	
Flow Rate	Field SOP 6.0	Р	N/A	None	0.1 feet/second	None	

Notes/Abbreviations:

- 1 Additional volume will be provided for laboratory QC samples (e.g., matrix spike, laboratory duplicate) as necessary.
- 2 Samples should be stored at a temperature ranging from 0°C 6°C, or analyze immediately.
- 3 Bromide, Chloride

CaCO₃ = calcium carbonate

P = Polyethylene



FIGURES



ATTACHMENT A-1

Standard Operating Procedures



ATTACHMENT A-1 STANDARD OPERATING PROCEDURES (SOPs) FOR FIELD ACTIVITIES

Rico-Argentine Mine Site Dolores County, Colorado

Submitted to:
Atlantic Richfield Company
La Palma, California

Submitted by:

AMEC Environment & Infrastructure, Inc.
Rancho Cordova, CA

June 2013



TABLE OF CONTENTS

SOP 1.0	Field Documentation and Sample Handling
SOP 2.0	Sample Collection Techniques and Data Collection Strategies
SOP 3.0	Field Measurements - Water
SOP 4.0	Equipment Decontamination
SOP 5.0	Investigation Derived Waste Disposal
SOP 6.0	Stream Flow Measurement and Surface Water Sampling
SOP 9.0	Operation and Maintenance of Automatic Water Sampling Equipment



SOP 1.0

Field Documentation and Sample Handling



SOP No.: 1.0 Revision: 01 Page 1 of 10

1.0 - FIELD DOCUMENTATION AND SAMPLE HANDLING

Purpose and Scope: The purpose of this document is to present procedures for field

documentation and sample handling. It includes a description of how to fill out a Daily Field Record (DFR), Sample Control Log, and Chain-of-Custody (COC). It also describes procedures for sample labeling,

handling, preservation, packaging, and shipping.

Equipment:

The following equipment will be needed depending on specific task and will be used, as appropriate, when packing or shipping samples:

Sample Bottles

Sample Labels

Custody Seals

Fine Tipped Permanent Markers

Nitrile gloves or other appropriate gloves

Sealable storage bags

Bubble wrap or appropriate packing materials

• Blue ice or double bagged ice

• Coolers suitable for sample shipment and holding ice

Strapping/packaging tape and shipping labels, if needed

· Camera with spare memory chip and batteries

Documentation:

DFR (attached)

Sample Control Log (attached)

COC Document (attached) or laboratory equivalent

Sampling Records Maps/plot plan

Camera

Photograph Log (attached)

1.1 FIELD AND SAMPLE DOCUMENTATION

Documentation of the conditions and procedures used to collect, treat, and handle samples and field data is one of the most important aspects of any sampling or monitoring program. Proper documentation provides sources to determine the integrity and applicability of the data. Carefully document all field activities in a field logbook or on data sheets. Field logbooks shall be bound with consecutively numbered pages and shall be written in with permanent ink. At the end of each field season, the original field log books and all original data sheets will be kept in the AMEC office, located in Rancho Cordova, California. Field activities shall be recorded in sufficient detail so that field activities can later be reconstructed from the notes. Any changes to the notes in the field logbook shall be made by drawing a single line through the incorrect material and initialing and dating the mark-out.



SOP No.: 1.0 Revision: 01 Page 2 of 10

1.1.1 Daily Field Record (DFR)

Documentation of observations and data acquired in the field provide information on sample acquisition, field conditions at the time of sampling, and a permanent record of field activities. Record field observations and data collected during the investigation with waterproof ink on DFR sheets (Attached). A new DFR should be completed for each day or when a separate phase of work is initiated. DFR should be single sided.

The DFRs will include the following information, as appropriate.

- Project and Task Number
- Project Name
- Location of sample (if samples are collected)
- Date
- Time
- Field Activity
- Weather Conditions
- Personnel Onsite, Company Name, and Time Onsite
- Personal Safety Checklist
- Description of Work Performed
- Description of Waste Generated

Information written within the area delineated "Description of Work Performed" should include the following:

- Sample identification number(s)
- Time of sample
- Description of sample
- Number and volume of samples
- Field observations
- List other associated paperwork related to the activity (e.g., boring log, sample control log, maps, etc.)
- Decontamination procedures



SOP No.: 1.0 Revision: 01 Page 3 of 10

Photographs should be taken of pertinent activities that occur during the investigation. These should include capturing images that clearly demonstrate that the goals of the project are being met. They should also be taken of any changes in procedures or unexpected findings that occur in the field. Items of scale should be included in the view of the photograph (i.e., ruler, clipboard, etc.). A running log of the photographs with a description of each photograph should be included on a photo log attached to the DFR. All photos should include the following information on the photo log: ID number generated by the camera, date the photo was taken, initials of the photographer, location of the photo, direction of view and any additional comments or descriptions.

Strike out changes or deletions in the field book or on the data sheets with a single strike mark and be sure that the original information remains legible. Each page should be completely filled without any blank lines, if necessary write "Not Applicable" or "NA" on blank lines. The field logbook or field data sheets should be signed daily by the author of the entries.

1.1.2 Sample Control Log

If samples are collected during the field investigation, a sample control log must be filled out documenting the sample location, study area, sample matrix, sample ID, sample date, sample time, sample collector, sample depth, sample type, code (whether the sample is a normal environmental sample or which type of quality assurance/quality control [QA/QC] sample it is), additional notes (i.e. sample turnaround time, COC remarks, details about the sample or analysis, etc.), which laboratory the samples were sent to and the date they were shipped.

1.1.3 Chain of Custody (COC)

During sampling activities, a "paper trail" of sample custody must be maintained from the time the samples are collected until laboratory data are issued. Information on the custody, transfer, handling, and shipping of samples should be recorded by the sampling personnel on an Atlantic Richfield COC form. If a project or task-specific COC form is not available (i.e., with specific analytes and analytical methods listed), an equivalent form provided by the destination laboratory can be used instead. A COC form will be completed for each set of samples collected daily. At a minimum, every COC will contain the following information:

- Sampling Personnel's name and signature
- Project name



SOP No.: 1.0 Revision: 01 Page 4 of 10

- Date and time of collection (corresponding to the respective field sampling record and sample control log)
- Field sample identification code and sample matrix
- Analyses/Methods requested
- Number of containers and any preservative used
- Signature of persons relinquishing custody, dates, and times
- Signature of persons accepting custody, dates, and times (exclusive of FedEx, UPS or similar service)
- Method of shipment
- Shipping tracking numbers/waybill identification number (as appropriate)

Additional Atlantic Richfield project tracking information to be completed on the COC includes the following:

- Name of the lead regulatory agency
- Name and contact information of the environmental business manager
- Name and contact information of the consultant and Project Manager
- Enfos proposal number and the stage and activity level of the project
- Level of data package requested

An example Atlantic Richfield COC is provided as an attachment and should be strictly followed as it is important that COCs are completed with consistent information. A copy of each COC form will be retained in the project files.

1.1.4 Sampling Records

Sampling records have been customized for each general sampling activity and are included in the respective SOPs. The associated sampling record should be filled out during the sampling process. Pertinent information varies with each type of sampling, but at a minimum, the following information should be filled out for each sample:



SOP No.: 1.0 Revision: 01 Page 5 of 10

- Project name
- · Project task description
- Location of sample
- Sample identification code (Sample ID)
- Time of sample collection
- Results of any field measurements, such as depth to water, pH, temperature, specific electrical conductance, dissolved oxygen, turbidity, discharge, etc.
- Instrument/s used to measure field measurements
- Any QA/QC samples that were collected
- Field observations, such as color, odor or texture of the sample, etc.
- Field test results (if applicable)
- Method of sampling
- Name and signature of sampler

If field measurements are recorded for a sample collected for laboratory analysis, the time recorded for the field measurements shall be consistent with the sample collection time. If a multiparameter sonde is deployed to continuously measure water quality parameters at a sampling location, water quality parameters for a sample collected for laboratory analysis can be obtained from the downloaded data files. The parameters selected to represent the sample extracted from the electronic data file will be recorded at the time closest to the sample collection time. For example, if a sample for laboratory analysis is collected at 10:36 and parameters were recorded by the multiparameter sonde at 11:00, the measurements recorded by the sonde at 11:00 should be used to represent the sample.

1.2 SAMPLE LABELING

After sample collection, the samples will be labeled with self-adhesive labels with all necessary information added using waterproof ink. Make sure the labels are completed so that the information is legible and consistent. At a minimum, each sample label will contain the following information:

- Project name
- Sample ID Date (mmddyy) and 24-hour clock time (hh:mm) of sample collection
- Analyses required



SOP No.: 1.0 Revision: 01 Page 6 of 10

- Preservatives, if applicable
- · Sampler's initials

The information on the sample label shall match respective record on the COC and sample control log.

Each sample will be assigned a unique identification code according to sample location, date, and depth (if applicable). For example, if a sample is collected from the 517 Shaft at a depth of 450 feet below the shaft collar on August 20, 2013, the sample ID will be "517Shaft450130820".

Field blanks and duplicates shall be labeled such that the sample location is not identified to the lab. All field QC samples will be given the sample identifier "QC", but will not identify the true QC sample type. To account for more than one QC sample collected on any given day, the sample identifier will be followed by a sequential number. For example, if a field duplicate sample is collected from the 517 Shaft, as given in the example above,, and it is the first QC sample collected on this day, the sample ID will be "QC1130820". The identity of field QC samples will be traceable through the sample control log and the project database.

1.3 SAMPLE HANDLING

General sample handling procedures shall include the following:

- Always make field measurements on a separate sub-sample, not on the sample that
 is sent to the laboratory for analysis. Discard the sub-sample after the
 measurements have been made.
- Do not use containers that have been used in the laboratory to store concentrated reagents or have been previously used as sample containers. Use only new containers that are certified clean by the manufacturer or laboratory for sample collection.
- For water samples, do not allow the inner portion of sample containers and caps to come into contact with bare hands, gloves, tubing or other objects.
- Keep sample containers in a clean environment away from dust, dirt, and fumes.
 Field personnel shall wear disposable nitrile gloves when collecting water samples.
 Gloves must be changed out between each water sample collected.
- Do not let any samples, including water, vegetation, or invertebrate samples, stand in the sun. Store all samples in coolers with blue or double bagged ice;



SOP No.: 1.0 Revision: 01 Page 7 of 10

 COC procedures will be strictly adhered to during sample collection, transportation, and laboratory handling to assure the identity of the samples. Improper sample and data handling and inadequate COC procedures affect the credibility and acceptability of analytical results, regardless of their accuracy or precision. COC documentation will document processing of the sample from the time of collection to the time of analysis.

If overnight storage of collected water samples is required prior to shipment to a laboratory, the samples will be stored in accordance to procedures described in Section 1.6.

1.4 SAMPLE PRESERVATION

Sample preservation will depend on the analytical method to be performed and the sample matrix. Preservation methods and preservatives for each analytical method and matrix will be presented in the St. Louis Tunnel Discharge Source Mine Water Treatability Study Quality Assurance Project Plan. The planned sample preservation activities, sample container size and type, and analytical methods should be confirmed with the laboratory well in advance of collecting samples.

For all water samples and select soil samples, the laboratory will supply clean, unused, and prepreserved sample containers as appropriate. If containers are preserved, the type of preservative should be clearly labeled on each bottle. Do not rinse out sample containers. The preservative (lab or field added) will be documented on the sample label and COC. Samples collected in non-laboratory certified clean containers (e.g., via split spoon, direct push, drive, or grab methods), will be decontaminated prior to use in accordance to procedures described in SOP 4.0, Equipment Decontamination.

1.5 SAMPLE PACKAGING AND SHIPPING

If samples are required to be chilled, they will be stored during the day, or overnight, in ice-cooled containers.

Samples collected during the morning may be temporarily stored in a refrigerator (if available) until shipment in the afternoon. All samples stored in the coolers or the refrigerator will be documented on the sample control log. When samples are being packaged for shipment, the procedures listed below will be followed.

1. Field personnel will visually screen each sample in the cooler for loose surface contamination, and confirm that each sample is listed on the sample control log and the COC.

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SOP No.: 1.0 Revision: 01 Page 8 of 10

- 2. Samples will be packed with abundant packaging material to minimize the potential for damage during shipment. If samples need to be chilled, they will be placed in sealable plastic bags and immediately placed on ice in an insulated cooler. Insulated coolers can be provided by the contract laboratories. Sample containers will be placed right side up in a cooler with double bagged ice for delivery to the laboratory.
- 3. The completed COC will be signed, scanned and emailed to the lab to inform them about the sample(s) they will be receiving. The scans will be saved for project records. Then, the COC will be placed in a plastic sealable storage bag which will be taped to the inside cover of the cooler. The COC form will be shipped with the cooler and serve as the legal documentation of sample custody for the field and laboratory.
- 4. If samples are to be transported overnight via Federal Express or United Parcel Service, all ice must be double bagged to prevent leakage. The lid of the cooler must be taped shut with custody seals. The cooler will then be taped shut using clear shipping tape. Failure to seal all potential leaks may result in rejection of delivery by the courier. If samples are shipped on a Friday then Saturday delivery stickers must be attached to the coolers on all four sides as well as the top. Make sure to check the overnight delivery space on the shipping papers. Affix the label on the top or side of the cooler.
- 5. Samples will typically be shipped to the laboratory daily. Copies of the completed COC will be kept in the field office by the field manager.
- 6. Sample shipment will be scheduled to prevent exceeding any required holding period. Failure to submit samples for analysis within the required holding times will prompt appropriate corrective and preventive action measures.

1.6 OVERNIGHT STORAGE

If the hold time allows, samples may be stored overnight as long as they are properly packaged, labeled, placed in a secure location. If chemical analysis is to be performed on the sample, it must be stored at no more than 6°C or 39°F, but above freezing. Samples will be kept in a cooler or refrigerator locked in a secure location and shipped the following day. When placing samples into the refrigerator, make sure it is plugged in and turned on and set at the appropriate temperature. Samples should not be kept for more than a week or longer than analytical holding times allow. If samples are kept overnight, chain of custody procedures must still be followed.



SOP No.: 1.0 Revision: 01 Page 9 of 10

1.7 REVISION LOG

Revision #	Author	Description of Change (Section #)	Date	Reviewer
01	ARC	Section 1.1.1 DFR should be single sided.	6/4/13	LL 6/6/13
		Section 1.1.4 Sampling Records – add text regarding field measure collection time and parameters recorded using the sonde.		
		Formatted Sample Control Log (1c)		



SOP No.: 1.0 Revision: 01 Page 10 of 10

ATTACHMENTS

- Daily Field Record (DFR)
- Sample Control Log
- Atlantic Richfield Chain-of-Custody (COC) Record
- Photograph Log



DAI	LY FIE	ELD RECORD)						
Project and Task Number:				Date:					
Project Name:				Field Activity:		,			
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DAILY FIELD RECORD (continued)						
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SAMPLE CONTROL LOG

Project Name:						Task Name:						
Project & Task No.			············		Week of:			Crew:				
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^{1.} Sample Types include: Grab, Composite, Incremental, or Autosampler

^{2.} Code includes: Normal Environmental (NE), Field Duplicate (FD), Field Blank (FB), Equipment Blank (EB), and Matrix Spike/Matrix Spike Duplicate (MS/MSD)

^{3.} Include notes such as: turnaround time, sample location details, handling notes, Chain-of-Custody remarks, etc.



Laboratory Management Program LaMP Chain of Custody Record

BP/ARC Project Name:

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Req Due Date (mm/dd/yy):		Rush TAT:	Yes	No_	
Lah Work Order Number					

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Lab Address:				City, State, ZÍP Code:										Consultant/Contractor Project No:													
Lab PM:					Lead Regulatory Agency:									Addre	988:							1					
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Lab Bo	ottle Order No:			Acc	ounti	ng Mo	de:		Pro	vision		00	C-BU		000	-RM			Email	EDD	То:						
Other	Info:			Sta	ge:				Ac	tivity:									Invoic	e To:		BP.	/ARC		Contracto	r	
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PHOTOGRAPH LOG

Project Name:					Task Name:
Project & Task No.:					Camera No:
Camera Assigned ID #	Date	Photographer Initials	Location	Direction of View	Additional Comments
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SOP 2.0

Sample Collection Techniques and Data Collection Strategies



SOP No.: 2.0 Revision: 1 Page 1 of 4

2.0 - SAMPLE COLLECTION TECHNIQUES AND DATA COLLECTION STRATEGIES

Purpose and Scope: The purpose of this document is to describe general sampling

techniques and data collection strategies.

Equipment: Nitrile gloves or other appropriate gloves

Measuring Wheel or Tape Measure

Flag markers

Hand-Held Global Positioning System (GPS) device;

Camera Marking flags Marking paint

Documentation:

Daily Field Record (DFR)

Photo Log Maps

Specific sample techniques, strategies, locations and frequency will be presented in the work plans. However, in the event that the work plans require that sample collection techniques and data collection strategies must be determined in the field (e.g. pre-investigation planning, mapping, waste sampling), the procedures within this SOP should be followed.

2.1 SAMPLE COLLECTION TECHNIQUES

Three basic types of sample collection techniques are: Grab, Composite, and Incremental Samples. These techniques are described below:

- A grab sample is defined as a discrete sample representative of a specific location at
 a given point in time. The sample is collected all at once at one particular point in the
 sample medium. The representativeness of such samples is defined by the nature of
 the materials being sampled. In general, as sources vary over time and distance, the
 representativeness of grab samples will decrease.
- A composite sample is a non-discrete sample composed of more than one sample
 collected at various sampling locations and/or different points in time. Analysis of
 this type of sample produces an average value and can in certain instances be used
 as an alternative to analyzing a number of individual grab samples and calculating an
 average value. It should be noted, however, that compositing can mask problems by
 diluting isolated concentrations of some hazardous compounds below detection
 limits.



SOP No.: 2.0 Revision: 1 Page 2 of 4

 Incremental sampling (IS) is a structured composite sampling protocol that reduces sampling error associated with compositional and distributional heterogeneity of the analyte of interest in soil or sediments. The IS protocol consists of defining sampling or decision units, collecting a minimum of 30 individual soil samples from randomly selected locations within each unit, and submitting the samples to the laboratory for processing (drying, compositing, sieving, and sub-sampling) in a specified manner prior to laboratory analysis.

2.2 DATA COLLECTION STRATEGIES

The number of samples that should be collected and analyzed depends on the objective of the investigation. There are three basic sampling strategies: random, systematic, and judgmental sampling. Each of the strategies is explained in the following:

- Random sampling involves collection of samples in a nonsystematic fashion from the entire site or a specific portion of a site.
- Systematic sampling involves collection of samples based on a grid or a pattern which has been previously established.
- Judgmental sampling involves collection of samples only from the portion of the site most likely to be contaminated.

A combination of these strategies is the best approach depending on the type of the suspected/known contamination, the uniformity and size of the site, and the level/type of information desired.

2.3 SAMPLE LOCATION DOCUMENTATION

Once a sample location is chosen and the sample has been collected, the location will be temporarily staked or marked until it has been surveyed. Additionally, 3 to 4 photos of the location should be taken so the location is well documented. The photos should be documented on a photo log (SOP 1.0 – Field Documentation and Sample Handling).

Wooden stakes, steel fence posts with safety caps, survey whiskers, pin flags with the name of the location written in permanent marker, or survey whiskers can be driven into the ground to show the location. It is not recommended that spray paint be used to mark locations as it may get washed off or brushed over by dirt and rocks. Spray paint may be used as a temporary location marker; however, the spray paint marker should either be surveyed or replaced as soon as possible so the location is not lost.



SOP No.: 2.0 Revision: 1 Page 3 of 4

For samples and activities that require high accuracy survey data such as the installation of borings for subsurface mapping, the installation of monitoring wells, piezometers, and monitoring ports for water level measurement, and the installation of surface monitoring monuments, survey activities will be subcontracted to a third party that has a current California survey license and is capable to surveying within a 100th of a foot. All surveys shall be completed using the most recent version of the State Plane Coordinate System. The surveyor will obtain accurate coordinates and elevations of the sample locations within several weeks after the installation activities.

If only sub-meter accuracy for vertical and horizontal survey information is needed, a hand-held GPS device may be used in place of a licensed surveyor to obtain general coordinates of locations and activities.



SOP No.: 2.0 Revision: 1

Page 4 of 4

1.4 REVISION LOG

Author	Description of Change (Section #)	Date	Reviewer
ARC	Minor edits.	6/5/13	LL 6/6/13
	Section 2.1- added Incremental Sampling		
		ARC Minor edits.	ARC Minor edits. 6/5/13



SOP 3.0

Field Measurements - Water



SOP No.: 3.0 Revision: 01 Page 1 of 15

3.0 - FIELD MEASUREMENTS - WATER

Purpose and Scope: The purpose of this document is to provide procedures for measuring

the water levels from wells and collecting field parameters in surface water and groundwater. It includes instructions on the setup, field

procedures, and how to fill out the associated field forms.

Equipment:

pH Meter and Electrode

Specific Electrical Conductance (SEC) Meter

Dissolved Oxygen (DO) Meter

Oxidation Reduction Potential (ORP) MeterThermometer or

Temperature Probe

Fluorometer

Fluorometer Sample Analysis Cuvette

Photometer and associated sample vials and reagents

Ion Specific Electrodes (ISE) and ISE Meter

Peristaltic Pump

0.45-micron Large-Capacity Filter Cartridges

Silicone Tubing
Polyethylene Tubing
Distilled Water
Deionized Water
Spray Water Bottles
1% Liquinox Solution
Sample Cup or Beaker

Calibration Standards for Each Meter

Miscellaneous Field Tools:

Socket for Flush-Mounted Wells

Cutting Shears

Spare Combination Locks Christie Box Opening Tool Flat Head Screwdriver

Extra Batteries Nitrile Gloves



SOP No.: 3.0 Revision: 01 Page 2 of 15

Documentation:

Daily Field Record (DFR)

Water Level Monitoring Record (attached)

Well Sampling Record (attached)

General Water Sampling Record (attached)
Multiparameter Meter Calibration Sheet (attached)

Single Point Calibration Sheet (attached) Multi-Point Calibration Sheet (attached)

Temperature Corrected Calibration Standards Data Sheet (attached) Individual Procedures for YSI Photometer Tests for Commonly Used

Test Methods (attached)

YSI Photometer Test Method Operating Ranges (attached)

This Standard Operating Procedure (SOP) describes the general methodology for water level measurement from wells, measuring field parameters in water, and performing field analytical tests on water samples. Field parameters typically consist of pH, specific electrical conductance (SEC), turbidity, oxidation reduction potential (ORP), temperature, and dissolved oxygen (DO). Analytical tests may be performed in the field and could include but are not limited to alkalinity, dissolved zinc, sulfide, iron, bromide, chloride, sodium, and Rhodamine. Refer to the manufacturer's recommendations for specific operational procedures and calibration requirements for each type of field instrumentation and field analytical methods described in this SOP.

All field measurements of water will be performed by appropriately trained field staff under the guidance of a California-licensed Professional Geologist or Professional Engineer.

3.1 SETUP AND EQUIPMENT CALIBRATION

Prior to taking any field measurements or performing field tests, sampling personnel will assemble all necessary equipment and calibration standards. All instruments to be used will be checked and/or calibrated per the manufacturer's instructions and as often as recommended by the manufacturer to ensure they are in proper working condition. Calibration data including the concentration of the calibration standard(s) and the calibration reading for the check standard(s) will be recorded on a Multiparameter Meter Calibration Sheet, Single Point Calibration Sheet, and/or a Multi-Point Calibration Sheet as applicable (attached).

3.2 WATER LEVEL MEASUREMENT

Water levels may be measured in monitoring wells, piezometers, and water supply wells or in other types of structures where water can accumulate (e.g. mine shafts, constructed wetland



SOP No.: 3.0 Revision: 01 Page 3 of 15

monitoring ports, ponds). For ease of use, "well" will refer to any structure in which the water level is being measured. Open the well by removing the lid on the well box and remove the well cap. When opening the well box and removing the cap, be sure to keep your head away from the top of the open casing to avoid inhaling any fumes that may reside within the well.

Decontaminate all water level measurement equipment as described in SOP 4.0 – Equipment Decontamination prior to inserting any instruments into the well.

Water level measurements will be referenced to a known elevation datum. The measuring point at the top of the well casing (generally the north side of the casing) or some other permanent reference point will be permanently marked and surveyed. Measurements will be consistently taken from the same marked point. Water levels will be measured with an electrical sounding device, a hydrocarbon interface measuring device, or equivalent device.

The static water level will be measured in each well using an electronic water level indicator. Measurements will be made by recording the depth-to-water (DTW) and repeating the measurement until at least two consecutive depth readings within 0.01-foot are measured. The final water level measurement for each well will be recorded in the field on a Water Level Monitoring Record.

When attempting to collect a DTW measurement, if a vacuum or a pressure buildup is detected upon opening the airtight well cap, an initial depth to water level will be obtained and the well will be allowed to equilibrate for approximately 3-5 minutes. After the field geologist or engineer has used professional judgment to determine that the water table is stable, another DTW measurement within the well will be obtained. Additional measurements will be obtained at 3-5 minute intervals until at least two consecutive depth readings are within 0.01-foot.

The field geologist or engineer may also measure the depth-to-bottom (DTB), or the depth to the bottom of the well by lowering a measuring device (e.g., sounding device) to the bottom of the well. If the sounding device has a "zero measuring point" at a place other than the tip of the probe, the difference in measurement will be added or subtracted from the reading so that the recorded value is an accurate measurement from top of casing to DTB.

At the completion of the DTW and possible DTB measurements, the field geologist or engineer will wipe down the down-hole equipment with a new paper towel to remove excess water or debris from the tool and decontaminate as appropriate.



SOP No.: 3.0 Revision: 01 Page 4 of 15

3.3 FIELD PARAMETERS

Generally, a multi-parameter water quality meter (YSI is the brand that is commonly used) will be used to measure field parameters. The following describes measuring field parameters of pH, SEC or EC, temperature, turbidity, ORP, and DO using an YSI meter or similar equipment.

3.3.1 pH

The general procedures for the operation, calibration, and maintenance of the field pH meter and its accessories are included in the instruction manual provided with the equipment. In addition, the instruction manual provides information regarding specific calibration requirements and user recommendations. Manufacturer's specifications and recommendations should be followed when using the pH meter.

Prior to use each day, the pH meter should be examined for cleanliness, for defects, and for any possible need of repair. The examination should include the battery and electrode. Once the pH meter is observed to be in correct operating condition, it should be calibrated using a minimum of a three-point calibration using 4.0, 7.0, and 10.0 pH standard solutions (purchased from a reputable vendor, and non-expired). pH meter should be calibrated to the temperature corrected standard solution values. Temperature corrected pH standard values are included in the Temperature Corrected Calibration Standards Data Sheet (attached). Calibration of the instrument should not be calibrated out of range. If calibration value is out of range do not except calibration. A value outside of acceptable range of the meter indicates a problem in the calibration process, standards used, or sensor malfunction. Instrument user manual should be referenced for troubleshooting procedures.

Prior to beginning the calibration, the expiration date for each of the calibration standards will be checked. Standard solutions that have expired will not be used and will be properly disposed in accordance with SOP 5.0 - IDW Disposal. A record of the pH reading for each concentration of standard and any calibration notes will be denoted on the Multiparameter Meter Calibration Sheet (attached).

3.3.2 Specific Electrical Conductance

The general operation, calibration, and maintenance for use of the SEC meter are included in the instruction manual provided with the equipment. In addition, the instruction manual provides information regarding specific calibration requirements and user recommendations.

Manufacturer's specifications and recommendations should be followed when using the conductivity meter.



SOP No.: 3.0 Revision: 01 Page 5 of 15

Prior to use each day, the SEC meter should be examined for cleanliness, for defects, and for possible need of repair. The examination should include the battery and the probe. Once the conductivity meter is observed to be in correct operating condition, it should be calibrated using a minimum standard solution of 1,000 micro-Siemens (μS/cm) at 25 degrees Celsius (° C) (purchased from a reputable vendor). When calibrating the SEC meter, temperature correction of the standard solution is not necessary because SEC is the electrical conductivity normalized to 25 °C. If electrical conductivity is calibrated on the meter, the meter should be calibrated to the temperature corrected calibration standard. Temperature corrected 1,413 μS/cm standard values are included in the Temperature Corrected Calibration Standards Data Sheet (attached). Calibration of the instrument should not be calibrated out of range. If calibration value is out of range do not except calibration. A value outside of acceptable range of the meter indicates a problem in the calibration process, standards used, or sensor malfunction. Instrument user manual should be referenced for troubleshooting procedures.

Prior to beginning the calibration, the expiration date for the calibration standard will be checked. Standard solutions that have expired will not be used and will be properly disposed of in accordance with SOP 5.0 – IDW Disposal. A record of SEC reading and any calibration notes will be denoted on the Multiparameter Meter Calibration Sheet.

3.3.3 Temperature

The operation procedure of the thermometer or temperature probe for use in the field is included in the instruction manual provided with the equipment. Prior to use each day, examine the thermometer/probe for cleanliness, defects, and any possible need of repair. Temperature calibration is done by the manufacturer.



SOP No.: 3.0 Revision: 01 Page 6 of 15

3.3.4 Turbidity

The general procedures for the operation, calibration, and maintenance of a field turbidity meter are included in the instruction manual provided with the equipment. In addition, the instruction manual provides information regarding specific calibration requirements and user recommendations. Turbidity meters used can either be part of a multiparameter unit or a single turbidity meter.

Prior to use each day, the turbidity meter should be examined for cleanliness, for defects, and for possible need of repair. The examination should include the battery. Once the turbidity meter is observed to be in correct operating condition, it should be blanked with a 0.0 NTU standard solution then calibrated using a standard solution close to the expected sample range (purchased from a reputable vendor). Prior to beginning the calibration, the expiration date for each of the calibration standards will be checked. Standard solutions that have expired will not be used and will be properly disposed in accordance with SOP 5.0 – IDW Disposal. Acceptance limits for each standard and any calibration notes will be denoted on the Multiparameter Meter Calibration Sheet.

If the turbidity meter reads in AU instead of NTU, then the sample is too turbid to collect a measurement. For documentation purposes, it should be noted that the meter is reading >500 NTU instead of noting the value in AU.

3.3.5 Oxidation Reduction Potential

The general procedures for the operation, calibration, and maintenance of the field ORP are included in the instruction manual provided with the equipment. In addition, the instruction manual provides information regarding specific calibration requirements and user recommendations.

Prior to use, examine the ORP meter for cleanliness, defects, and any possible need of repair. The examination should include the battery and probe. Once the ORP meter is observed to be in correct operating condition, it should be calibrated using a minimum standard solution of 100 milliVolts (mV) (purchased from a reputable vendor). Temperature corrected ORP standard values for Aurical Company and Zobell's standards are included in the Temperature Corrected Calibration Standards Data Sheet (attached). If other another ORP calibration standard is used, the temperature corrected values from the manufacture must be obtained prior to use. If calibration value is out of range do not except calibration. A value outside of acceptable range of



SOP No.: 3.0 Revision: 01 Page 7 of 15

the meter indicates a problem in the calibration process, standards used, or sensor malfunction. Instrument user manual should be referenced for troubleshooting procedures.

Prior to beginning the calibration, the expiration date for the calibration standard will be checked. Standard solutions that have expired will not be used and will be properly disposed of in accordance with SOP 5.0 – IDW Disposal. A record of the ORP reading and all calibration notes will be denoted on the Multiparameter Meter Calibration Sheet (attached).

3.3.6 Dissolved Oxygen

The general procedures for the operation, calibration, and maintenance of a field DO meter are included in the instruction manual provided with the equipment. In addition, the instruction manual provides information regarding specific calibration requirements and user recommendations.

Prior to use, examine the DO meter for cleanliness, defects, and any possible need of repair. The examination should include the battery and probe. Once the DO meter is observed to be in correct operating condition, it should be calibrated using distilled water and the barometric pressure of the atmosphere where the DO is being collected. If calibration value is out of range do not except calibration. A value outside of acceptable range of the meter indicates a problem in the calibration process, standards used, or sensor malfunction. Instrument user manual should be referenced for troubleshooting procedures. All calibration notes must be recorded on the Multiparameter Meter Calibration Sheet (attached).

DO is generally calibrated in percent (%) but the sample readings must be recorded in mg/L. DO levels vary based by temperature, true barometric pressure, and salinity. True barometric pressure has not been corrected to sea level. Note that most weather service readings are not true and have been corrected to sea level and must be uncorrected. An approximate formula to convert corrected barometer pressure to the true barometer pressure is presented below.

The general saturation levels range from 8 to 14 mg/L DO. If the meter reads above the saturation level for the current temperature and pressure, it should be recalibrated. If it is still out of range, the membrane and solution should be changed.



SOP No.: 3.0 Revision: 01 Page 8 of 15

3.3.7 Pressure Transducer

The general procedures for the operation, calibration, and maintenance of pressure transducer used to measure changes in water levels are included in the instruction manual provided with the equipment. In addition, the manual provides information regarding specific operational parameter that must be programmed prior to using the pressure transducer. These parameters could include but are not limited to site elevation, latitude, and density of water in order to convert the pressure measurement into a water depth or water level.

Field personnel should be familiar with software required for programming and downloading data from the pressure transducers prior to use.

3.3.8 Multiparameter Meters

Multiparameter meters such as YSI 556 MPS, YSI 6920 multiparameter sondes, Multiparameter Troll 9500, or similar may be used for grab or continuous water quality monitoring. Prior to use, instruction manual provided with the equipment should be review. The general procedures for the operation, calibration, and maintenance of multiparameter sondes are included in the instruction manual provided with the equipment.

Field personnel should be familiar with software required for programming and downloading data from the multiparameter meters prior to use.

If possible calibration checks will be performed approximately weekly by measuring the monitoring location water quality parameters with calibrated multiparameter meter and compared to the in-situ multiparameter sonde water quality measurements. If the relative percent difference between the sonde and the calibrated meter is greater than 20%, the sensor should be further evaluated by placing the sensor in a known calibration standard and recalibrated if necessary.

This calibration check may not be applicable to certain sensors, such as ORP. Similar or identical calibrated ORP sensors have shown to read significantly different values (up to 100 - 150 mV) in the same source water and read the same value in a calibration standard. Variations in ORP measurements can be due to lack or low concentration of redox active agent in the environmental water (YSI Environmental, 2005). In general, ORP sensors with long term exposure to sample water will provide the most accurate ORP measurement because of the length of time required for the ORP electrode to equilibrate with source water. However, maintenance should be performed periodically on sonde ORP sensor electrode to ensure field



SOP No.: 3.0 Revision: 01 Page 9 of 15

consistency and accuracy. Sensor electrode cleaning should be performed in accordance with manufactures' recommendations.

3.3.9 Water Quality Probe Cleaning, Maintenance, and Sensor Replacement

Water quality sensors should be maintained per the manufactures recommendations. Special care should be implemented to sensors exposed to fouling environments (anoxic, caustic, etc.). If visual fouling is observed on sensors, sensors should be cleaned to ensure field consistency and accuracy.

Approximately yearly, annual factory maintenance will be performed to the water quality meters. Meters used for continuous water quality monitoring may require more frequent factory maintenance and sensor replacement. The sensor replacement schedule will be contingent on frequency of sensor use.

3.3.10 Rhodamine

A field or in-situ fluorometer could be used to measure Rhodamine dye concentrations during tracer studies. The operation and calibration procedure for the fluorometer for use in the field is included in the instruction manual provided with the equipment. Prior to use each day, examine the fluorometer for cleanliness, defects, and any possible need of repair. The examination should include the battery and probe.

Once the fluorometer is observed to be in correct operating condition, it should be calibrated using at least a two point calibration. The standards should target the lower and upper operation range of the instrument. If a YSI 6130 optical Rhodamine fluorometer sensor is used, the lower range calibration standard will be deionized water to target 0 mg/L and Rhodamine dye used for the tracer study will be used to create a standard in the range of 125 – 175 mg/L to target the upper operation range of the sensor. Follow the operating instructions provide in the instrument manual for proper calibration. A record of the fluorometer calibration, including all readings and calibration notes shall be denoted on the Multi-Point Calibration Sheet (attached).



SOP No.: 3.0 Revision: 01 Page 10 of 15

3.3.11 Tagout

If any of the above water quality meters are found to be above or below the range of concentration for check standard, the equipment must be locked out and tagged out so it will not be used inadvertently. A replacement meter shall be obtained and properly calibrated while the out of range equipment is repaired.

3.3.12 Procedures for Testing a Sample

Samples will be tested for the above water quality parameters by triple-rinsing a small container with the sample water before filling the container with the sample to be tested or by placing the multiparameter meter with probe guard installed directly into sample water. If sample container is filled to measure parameters, ensure all the appropriate probes will be submerged. The probes shall remain in container or source water until parameters stabilize.

In some cases a flow-through cell may be used while collecting water quality parameters. If a flow-through cell is used it must be decontaminated in between each sample location (see SOP 4.0 – Equipment Decontamination). Do not use detergents when decontaminating probes. Only rinse probes with fresh or distilled water.

Once the water quality readings have stabilized, but before the temperature of the sample begins to change (less than 5 degrees Celsius difference from the initial temperature reading) because of the ambient temperature, the values for each parameter will be recorded on the appropriate sampling record (attached). If the sampling and monitoring program requires the measurement of aerobic and anaerobic sample water, the aerobic samples should be measured before the anaerobic water samples. If anaerobic sample water is measured first, the response to changes in ORP will be very slow and it is likely that ORP will not stabilize.

3.4 FIELD ANALYTICAL METHODS FOR ALKALINITY, ZINC, SULFIDE, AND IRON

Field measurement of alkalinity, zinc, sulfide, and iron can be made with a YSI 9500 Photometer. The photometer operation procedures for use in the field are included in the instruction manual provided with the meter. Prior to use each day, the photometer should be examined for cleanliness, defects, and any possible need of repair, or if the battery or test vials need to be replaced.

The field test methods for alkalinity, zinc, sulfide, and iron are attached which include the respective reagent's and testing protocol for each method. Prior to running a photometer field test, analyze a blank sample by filling a test vial with the water to be sampled to allow for the



SOP No.: 3.0 Revision: 01 Page 11 of 15

photometer to compensate for the inherent color of the sample. Each test method has its own reaction time period and sample should be analyzed immediately after the reaction period has lapsed. If the concentration detected using the desired field method exceeds the operating range of the photometer for a given method, the sample shall be diluted and re-analyzed. Dilution procedures are described in Section 3.6.

Calibration checks should be performed at least weekly to test the operational performance of the photometer. The calibration check will be performed by testing the transmittance of four known color standard. The table below describes the color standards with the corresponding wavelength and transmittance value.

Standard No.	Standard Color	Wavelength (nm)	Transmittance (%)			
33783/A	Clear	0	0			
33783/B	V-11	450	47.1			
	Yellow	500	68.3			
2272210	Dinle	550	51.6			
33783/C	Pink	570	70.3			
33783/D	Croon	600	60.9			
	Green	650	44.5			

To perform the calibration test select Test Method Phot.0. for Transmittance. First run standard 33783/A as the blank. Test the remaining standards for transmittance using the ↑ or ↓ key to select the appropriate wavelength designated in the table above for each color standard and take photometer reading in usual manner per photometer instructions. Record and compare transmittance results to the table above and if the transmittance recorded is greater than or less than 2%, the calibration of the meter is not in operable range and troubleshooting shall be conducted. Standards should be retested confirming the correct wavelength for each standard was selected. If transmittance results are still not within range the photometer shall be locked out and tagged out using the procedures described in Section 3.3.11 and serviced by a YSI service center for proper calibration.

3.5 FIELD ANALYTICAL METHODS USING ION SPECIFIC ELECTRODES

Concentration of various ions in aqueous solution can be measured in the field using Ion-Specific Electrodes (ISE). The operation procedure for the ISE is included in the instruction



SOP No.: 3.0 Revision: 01 Page 12 of 15

manual provided with the equipment. Prior to use each day, examine the ISE for cleanliness, defects, and any possible need of repair.

If the electrodes are in frequent use, the membrane surface can be left exposed to open air protected by a clean beaker. For long term storage, membrane on the electrode should be protected by covering the membrane with the cap provided with the electrode.

lonic strength adjustment buffers should be added to all samples and calibration standards to normalize the ionic strength of the solutions to minimize interferences.

Once the ISE is observed to be in correct operating condition, establish a multi-point calibration curve. ISE calibration standards are prepared at known concentrations. Typically the calibration standards created will be 1000 parts per million (ppm), 100 ppm, 10 ppm, 1 ppm, and 0.1 ppm. However, if the concentration range is known, calibration standards will be created closely bracketing the know concentration range. The measured mV readings for each standard solution is plotted against the actual activity on a logarithmic X-axis. The calibration curve should be linear in terms of mV response per decade of concentration change. If the calibration is not linear, troubleshooting should be performed as discussed in the operating instructions.

A record of the ISE calibration, including all readings and all calibration notes shall be denoted on the Multi-Point Calibration Sheet (attached).

3.6 SAMPLE DILUTION

A sample will have to be diluted if the concentration is detected above the operating range of the respective testing equipment. The dilution of sample may be an iterative process until the proper dilution ration is obtained. The goal of dilution is to obtain a reading within the working range of the instrument; the concentration reading is neither below the detection limit, nor above the working range. For example, a 1:100 sample dilution may conducted first by adding 1 part sample to 99 parts deionized water for a total of 100 parts (1:100). If the resulting value is near or below the detection limit, a dilution of 1 part sample to 49 parts deionized water for a total of 50 parts (1:50) will be conducted. The instrument reading of the diluted sample is multiplied by the dilution factor to determine the final concentration. Record the results on the Sampling Record along with the dilution factor (i.e., ratio).



SOP No.: 3.0 Revision: 01 Page 13 of 15

3.7 REFERENCES

YSI Environmental, 2005. Tech Note: Measuring ORP on YSI 6-Series Sondes: Tips, Cautions and Limitations.



SOP No.: 3.0 Revision: 01 Page 14 of 15

3.8 REVISION LOG

Revision #	Author	Description of Change (Section #)	Date	Reviewer
01	ARC	Section 3.3 – revised calibration procedures and DO calibration procedures to calibrate using true barometric pressure Section 3.3.7 – added section for use of pressure transducers Section 3.3.8 – added section for use of Multiparameter meters Section 3.3.9 – added section on probe maintenance procedures Section 3.3.10 – added calibration standards for YSI Rhodamine sensors Section 3.4 – revised photometer field methods and included calibration check procedures Section 3.5 – revised ISE field methods Section 3.6 – revised sample dilution procedures. Revised field forms and added Multi-Point Calibration Sheet	6/5/13	LL 6/6/13



SOP No.: 3.0 Revision: 01 Page 15 of 15

ATTACHMENTS

- Water Level Monitoring Record
- Well Sampling Record
- Grab Groundwater Sampling Record
- Multiparameter Calibration Sheet
- Single Point Calibration Sheet
- Multi-Point Calibration Sheet
- Individual Procedures for YSI Photometer Tests for Commonly Used Test Methods
- YSI Photometer Test Method Operating Ranges



SOP 4.0

Equipment Decontamination



SOP No.: 4.0 Revision: 01 Page 1 of 5

4.0 - EQUIPMENT DECONTAMINATION

Purpose and Scope: The purpose of this document is to describe procedures for equipment

decontamination. It describes decontamination methods and provides

specific procedures for decontaminating drilling and excavation equipment, submersible pumps, decontamination for the collection of

equipment blanks, and water level meters.

Equipment:

Steam Cleaner

5-gallon buckets with lids

Bucket labels Brushes

Distilled water Potable water Spray bottles Paper towels

Liquinox® or other Non-Phosphate Cleaning Solution (not Alconox®)

10 mil visqueen

Documentation:

Daily Field Record (DFR)

4.1 DECONTAMINATION PROCEDURES

Decontamination procedures described in this section are applicable to non-dedicated, non-disposable sampling equipment. The following subsections describe the methods of decontamination and procedures for decontaminating specific types of sampling equipment.

4.1.1 Decontamination Methods

All sampling equipment must be decontaminated after it arrives onto the site and before each sampling operation. This includes subcontractor equipment. Decontamination onsite will use one of the methods below:

- Three-Step System
- Steam Cleaner



SOP No.: 4.0 Revision: 01 Page 2 of 5

The procedures for decontamination using the three-step system or steam cleaner are described in the following subsections. The exception to using the three-step system or a steam cleaner for decontamination is when cleaning a water level meter. This is described in Section 4.1.2.4 of this SOP.

4.1.1.1 Three Step System

The three step decontamination system consists of washing the sampling equipment: (1) in soapy water using a non-phosphate (Liquinox®) solution, (2) rinsing with potable water and (3) rinsing again with distilled water. The Liquinox® solution will be mixed in accordance with the manufacturer's recommendations. Equipment will be washed in a row of three containers. Depending on the equipment to be decontaminated, spray bottles containing the applicable solutions may be used. Hard bristle bottle brushes may be used to remove mud and debris prior to the three step system with an optional fourth container. Sample equipment should be allowed to drain dry after the final distilled water rise. Decontamination water will be disposed of according to procedures described in SOP 5.0 – Investigation Derived Waste Disposal.

4.1.1.2 Steam Cleaner

The steam cleaner will be supplied by a subcontractor and operated according to the manufacturer's recommendations. It will be capable of generating a working pressure of approximately 1,500 to 2,000 pounds per square inch (psi), a discharge rate of 3 to 5 gallons per minute (gpm), and an operating temperature of approximately 130 to 150 degrees Fahrenheit (°F).

The steam cleaner will be used within a decontamination station designed to capture all of the water. The decontamination station may be mounted on a portable trailer or constructed onsite and will be supplied or built by a subcontractor. If constructed, the on-site decontamination area will be lined and bermed with two layers of 10 mil visqueen to contain rinsate from steam cleaning operations. If appropriate, the decontamination area will be designed to allow heavy equipment (backhoe, drilling rig, and support vehicles) to drive onto the visqueen. During operation of the steam cleaner, the field engineer or geologist will establish and maintain an exclusion zone. Decontamination water will be retained and disposed according to procedures described in SOP 5.0 – Investigation Derived Waste Disposal.



SOP No.: 4.0 Revision: 01 Page 3 of 5

4.1.2 Sampling Equipment

The following subsections provide specific details for decontaminating drilling and excavation equipment, submersible pumps, equipment blanks, and water level meters.

4.1.2.1 Drilling and Excavation Equipment

Drilling and excavating equipment, including backhoe buckets, drill bits, casing, augers, and tools or other equipment that have come in contact with potentially impacted soils or water will be cleaned between each location, as appropriate. After completion of each boring, drill casing or augers, drill bits and drill rods will be transported by truck to the steam cleaning area. Drill casing from the monitoring well drilling procedures will be lifted from the support truck and cleaned within the decontamination station. Heavy tooling with edges that can damage the decontamination area will be placed on lumber in the decontamination area for cleaning. Rinsate collected in the decontamination area will be retained and disposed according to SOP 5.0 – Investigation Derived Waste Disposal.

4.1.2.2 Submersible and Bladder Pumps

If a non-dedicated submersible pump is used, it will be cleaned prior to use and between sampling locations using the three-step system. First, the pump intake device will be submersed into non-phosphate cleaning solution (Liquinox®) and recycled within a bucket for at least 30 seconds. Second, the pump will be submersed into a bucket containing potable water and recycled within the container for at least 30 seconds. The second step should be performed sufficiently rinse the suds from the pump. The third step involves rinsing the pump within a bucket filled with distilled water using the same method as Steps 1 and 2.

If a non-dedicated bladder pump is used, it will first be disassembled and decontaminated using the three-step system. If so equipped, the disposable bladder will be removed and replaced with a new bladder. The used bladder will be disposed using project procedures for disposing solid waste. Then, the bladder pump will be assembled and rinsed with distilled water.

4.1.2.3 Equipment Blanks

As appropriate, equipment blanks may be collected after decontamination of the sampling equipment during sampling activities to provide an additional check on possible sources of contamination related to field sampling instruments. Equipment blanks are prepared using distilled or deioniezed water that is poured through or over the sampling device. The collected rinse water is then transferred to the appropriate sampling container(s) and handled in a manner



SOP No.: 4.0 Revision: 01 Page 4 of 5

similar to the associated field samples as described in SOP 1.0 – Field Documentation and Sample Handling.

4.1.2.4 Water Level Meters

Water level meters will be decontaminated using a two-step system. This system consists of a spray bottle containing non-phosphate detergent (Liquinox®) mixed with water and a spray bottle containing distilled water. The Liquinox® solution will be mixed in accordance with the manufacturer's recommendations. The soapy water will be sprayed on the portion of the water level meter that was submerged and then rinsed by spraying distilled water until all suds are removed. The submerged portion of the water level meter will then be wiped down with a paper towel. If residual dirt or other contaminants remain on the water level meter after being rinsed, the above steps will be repeated using a brush to remove the remaining debris. Rinse water from the above procedures will be captured in a bucket or other appropriate container, labeled, and disposed in accordance with procedures described in SOP 5.0 – Investigation Derived Waste Disposal.



SOP No.: 4.0 Revision: 01 Page 5 of 5

4.2 REVISION LOG

Revision #	Author	Description of Change (Section #)	Date	Reviewer
01	ARC	General formatting and editing	6/4/13	LL 6/6/13
		Section 4.1.2.3 – modified equipment blank sampling procedures		



SOP 5.0

Investigation Derived Waste Disposal



Standard Operating Procedures
Investigation Derived Waste Disposal

SOP No.: 5.0 Revision: 01 Page 1 of 6

5.0 - INVESTIGATION DERIVED WASTE DISPOSAL

Purpose and Scope: The purpose of this document is to present procedures for containment

and disposal of investigation derived waste such as soil, water, and

materials.

Equipment: Buckets, containers with covers for soil and water

(e.g., 55-gallon drums, 20-yard roll-off bins, Baker Tanks™)

Waste disposal labels

Appropriate sample containers and sampling equipment

Miscellaneous tools Safety Equipment

Documentation:

Daily Field Record (DFR)

Waste Tracking Log (attached)

Maps/plot plan

Camera

The procedures below are to be followed for investigation derived waste consisting of water, soil, materials such as personal protective equipment (PPE) or disposable sampling equipment, and liquid waste such as waste calibration solution and field test reagent waste. Investigation derived groundwater will be generated from well development and purging activities. Investigation derived waste water will be generated during decontamination activities. Investigation derived soil will be generated from soil borings.

All containers containing waste will be kept closed and sealed at all times unless actively adding waste. Each container must have a visible and legible label present. Labels will be constructed of weather-resistant vinyl and waterproof ink markers will be used to add information in the field. All empty containers must have a label that indicates that the container is empty. Prior to filling any waste containers, the sampler will replace the empty label with a label that describes the source of the waste (well or boring ID), the contents (soil or water), date accumulation started, date accumulation finished, and a name and contact information of the generator. The location of the waste generated will be documented on a waste tracking log (attached).



Standard Operating Procedures Investigation Derived Waste Disposal SOP No.: 5.0 Revision: 01 Page 2 of 6

5.1 WATER DISPOSAL PROCEDURES

Groundwater produced during the well development and purging activities will be discharged to the ground surface near the well for evaporation and infiltration or into one of the storage ponds. Water will be discharged in a manner that prevents erosion, pooling of water, or migration to a surface water body and will be performed in accordance with the HSSE Program document and the TSHASP. Measures to prevent erosion or migration may consist of installing silt fencing down slope of discharge areas or transporting and land applying water in a more appropriate location. If surface discharge is not practicable or allowed, water may be containerized (e.g. in a pipe, hose, or drum) and transported to an onsite treatment system, or may be transported off-site for appropriate disposal.

Waste water produced from decontamination activities will be disposed in the same manner as described above. This includes Liquinox® (a non-phosphate detergent) that is mixed with water using the manufacturer's recommendations. Alconox® or other detergents containing phosphates will not be used on site. If other cleaning agents are used during decontamination, the field engineer or geologist will contact the Project Manager for guidance on the proper disposal procedure.

It is not anticipated that investigation-derived waste water will be transported off site.

5.2 SOIL DISPOSAL PROCEDURES

It is anticipated that most soil investigations will be performed in areas that have unconsolidated material at the surface that was left behind from previous site activities (i.e., mining, construction). Any soil or mud developed during the drilling or excavation activities are expected to have similar characteristics as the disturbed material that exists in the vicinity of the investigation. Therefore, if disturbed material already exists at the surface, any soil or mud developed during the investigation will be spread evenly in the immediate vicinity. The material will be spread in a manner that has a low profile as to prevent windblown dust from occurring. These soil disposal activities will be performed in a manner that prevents migration to a surface water body and in accordance with the HSSE Program document and the TSHASP.

If soil and mud produced during the investigation is suspected to contain other contaminants (e.g., petroleum odors, ethanol odor), the field Engineer or Geologist will contact the Project Manager for guidance. Exceptions to the above soil disposal procedures will be addressed on a case-by-case basis.



Standard Operating Procedures
Investigation Derived Waste Disposal

SOP No.: 5.0 Revision: 01 Page 3 of 6

5.3 MATERIAL DISPOSAL PROCEDURES

Used PPE, sampling devices that contact with source water, and all other disposable equipment, including items such as rope and non-hazardous well construction materials will be disposed in the onsite municipal solid waste trash receptacle. The exception is for the disposal of equipment that has come in contact with contaminants that are suspected to be non-native to the area or those that are known to be hazardous (e.g., ethanol, diesel fuel, etc.). If this situation exists, the field engineer or geologist will contact the Project Manager for guidance.

5.4 LIQUID WASTE

Liquid investigation derived waste generated at the site will include waste calibration solutions (pH buffers, specific electrical conductance, oxidation reduction potential, turbidity) and field test reagent waste. Liquid waste will be stored for disposal in containers that are sealed and labeled. These containers will be stored onsite on secondary containment and later transported to an appropriate offsite disposal facility.

Liquid waste will be segregated in containers based on chemical compatibility. The Health and Safety Manager is responsible for reviewing material safety data sheets, evaluating chemical compatibility of liquid wastes and determining storage options for liquid wastes generated.

5.5 OFFSITE FACILITY DISPOSAL PROCEDURES

Offsite disposal of investigation derived waste is not expected. However in the event that it is needed, the location and quantity of the waste that is generated will be documented on a map and Waste Tracking Log (attached).

Offsite disposal of waste will be performed in accordance with appropriate Federal, State, and local regulations. A sample of the waste to be disposed at an offsite facility will be collected and submitted to a laboratory for analysis. Analytical results of the sample will then be sent to the disposal facility where a waste profile will be generated. The profile will be reviewed and signed by a designated Atlantic Richfield representative. The U.S. EPA will then be notified of all types and quantities of waste prior to its shipment off site.

Upon approval of the waste profile, an appropriate manifest (Hazardous or Non-Hazardous) will be completed. All waste manifests will be reviewed and signed by a designated Atlantic Richfield representative. The truck driver transporting the waste will also sign and keep the manifest in his presence at all times while transporting the container to the disposal facility. The



Standard Operating Procedures Investigation Derived Waste Disposal SOP No.: 5.0 Revision: 01 Page 4 of 6

truck driver will be responsible for adhering to all Department of Transport (DOT) rules and regulations for the transport of waste on public roads.



Standard Operating Procedures Investigation Derived Waste Disposal SOP No.: 5.0 Revision: 01 Page 5 of 6

5.6 REVISION LOG

Revision #	Author	Description of Change (#)	Date	Reviewer
01	ARC	Section 5.3 – revised text to say that PPE, disposable sampling equipment will be disposed in municipal solid waste trash receptacle. Section 5.4 – added section to describe handling of liquid waste.	6/4/2013	LL 6/6/13



Standard Operating Procedures
Investigation Derived Waste Disposal

SOP No.: 5.0 Revision: 01 Page 6 of 6

ATTACHMENT

Waste Tracking Log

Waste Tracking Log

Rico-Argentine Mine Site - Rico Tunnels Operable Unit OU01 Rico, Colorado



Date	Waste Type and Volume	Source Location	Container Type and Volume	Number of Containers	Storage Location
	4.4.4				·



SOP 6.0

Stream Flow Measurement and Surface Water Sampling



SOP No.: 6.0 Revision: 01 Page 1 of 14

6.0 - STREAM FLOW MEASUREMENT AND SURFACE WATER SAMPLING

Purpose and Scope: The purpose of this document is to provide a general outline for

developing site specific procedures for collection of representative surface water samples measurements in small streams, small rivers or

ponds and lakes.

Equipment:

Surface Water Sample Collection Devices:

Dip sampler;

Discrete depth sampler and associated equipment;

Peristaltic pump, power supply and associated equipment;

Directional Compass:

25-foot Steel Tape and 100-foot Flexible Tape Measure;

Survey stakes, flagging, hammer;

Marking Buoys, pre-stretched line and anchors; Boat or Raft (deep River or Pond/Lake Sampling);

Appropriate Line;

USCG Approved Type III Life Vests;

Vertical Staff Gauge:

3-inch, schedule 40 PVC Pipe, length to be determined

Electronic Depth Gauge;

Volumetric Flow Measuring Structure (Flume)

Sample containers (cleaned and provided by the laboratory);

ice chests and blue or double bagged ice;

Tarps:

Miscellaneous tools;

Safety Equipment,

Hand-Held Global Positioning System (GPS) device; and

Hip boots and Knee-high water tight boots.



SOP No.: 6.0 Revision: 01 Page 2 of 14

Documentation:

Daily Field Record (DFR);

Maps:

Digital Camera and Photo Log;

Sample Control Log:

Atlantic Richfield Chain-of-Custody (COC) form or laboratory equivalent;

Multiparameter Calibration Sheet (or other means to document

instrument calibration);
Single Point Calibration Sheet;
General Water Sampling Form; and

Stream Flow (Discharge) Measurement Form (attached).

6.1 STREAM FLOW MEASUREMENT

Small stream and river volumetric flow can be calculated with measurements of the stream cross-sectional area and the velocity of flow through that area using the following formula.

 $Q = V \times A$

Where.

Q = Discharge (in cubic feet per second)

V = Velocity (in feet per second)

A = Area (in square feet)

The area of the cross-section through which water is flowing will be determined by one or more techniques based on the overall general size of the stream (width and depth) and water velocity. A staff gauge (graduated into feet and tenths of feet (meters and centimeters) can be used to directly measure depths of shallow streams and rivers at select points perpendicular to the stream flow. If the bottom profile of the stream or river is undulating or complicated in some manner, the sum of the volumetric flows of the individual areas making up the cross-section can determine the overall volumetric flow rate. This will require calculating the individual areas and determination of corresponding velocities in those areas. For relatively simple geometries, a simple depth measurement and velocity determination can be directly made. For complicated geometries and deep water (greater than approximately 2.5 feet) multiple velocity readings, using one of a number of velocity specific and calibrated electronic or magnetic flow meters will be required.

6-2



SOP No.: 6.0 Revision: 01 Page 3 of 14

An alternative method for directly reading stream or river volumetric flows, at locations that require repeated sampling, may be to install a permanent Weir or Flume that can be used to channel flow and read volumetric flows directly. If this method is utilized, it will require plans and specifications for the design and construction of the structure.

The proper collection of representative surface water samples will also be dependent on the geometry and depths of the surface water to be sampled and the contaminant of concern. Surface water can be sampled through direct filling of contaminant specific sample containers or through collection of the sample in a pre-defined sample collection device where the sample is then transferred to the sample container. Generally, sampling of surface water from ponds and lakes do not require volumetric flows but will require knowledge of the total depth of the pond or lake and a predetermined knowledge of the depths from which samples are to be collected.

The choice of the proper location to collect a surface water sample, the method to measure areas and velocities and the proper choice of the materials of construction and type of flow meter and sample collection device is site and contaminant-specific and shall be defined in the work plans.

All work performed determining areas, velocities and collection of representative samples should be thoroughly documented on a DFR using diagrams. Photographs and a photo log will also be used to document the methods used for measuring flow.

6.1.1 Choosing a Transect Location

Stream flow measurements are performed along a transect of the stream. The transect location should include an area of moving water that can be waded and in an area of channelized flow. Hip boots or Knee-high water tight boots will be used for wading in streams. The transect location should be chosen based on a variety of general criteria ranging from point-source outfalls of concern, stream morphology, accessibility, safety concerns, and the location of preestablished sample locations. Once chosen, a transect location should be documented to provide a basis for repetition and comparison with previous or future sample events.

Stream specific criteria for selecting a transect location include looking for particular characteristics such as:

6-3



SOP No.: 6.0 Revision: 01 Page 4 of 14

- · a well defined and stable stream bank;
- · few obstructions in the channel; and
- no eddies or still water.

Conversely, turbulent water should also be avoided, if possible. The stream should be free flowing and unrestricted by obstructions upstream or downstream, which might cause flow diversion or flow backup. A smooth streambed profile, one of relatively consistent depth across its width, is optimal. The depth of the stream must be adequate for the determination of a flow velocity and subsequent collection of the surface water sample without disturbing the stream bottom sediment.

For purposes of reproducibility, any likely movable objects within the stream bed, which may interfere with the reproducibility with subsequent sample collection events should be removed, if possible and allowable. Removal of channel obstructions, (i.e., woody debris, rocks, or other obstructions), should be performed to allowed sufficient time for stream flow re-stabilization before flow measurements are recorded.

6.1.2 Setup

Once a transect location is selected, the stream flow equipment should be laid out as close to the transect as safety allows.

- Lay out tarps near the area where readings are to be performed, one for equipment, and one for staff seating and miscellaneous supplies.
- Unload equipment and setup the workstation, allowing for easy access to needed materials.
- If contaminants are expected (such as pathogens), establish a decontamination area with another tarp where staff will be exiting the stream. Place decontamination supplies (sprayer bottles with bleach solution and distilled rinse water) in this area.
- If the banks of the stream are steep, place a ladder against the bank for safe ingress and egress.

6.1.3 Setting up the Transect

If the stream to be sampled is more than a few (five) feet across and the bottom profile of the stream is geometrically complicated, a transect for defining the area of the stream (by defined



SOP No.: 6.0 Revision: 01 Page 5 of 14

small sub-areas of depth) will be defined and measured in the field. The following procedures describe the process for setting up the transect.

- Setup the transect endpoints by driving a stake into the ground on each side of the stream. The resulting transect should be at right angles to the stream flow.
- Stretch a line (polyester pre-stretched line) across the stream and fasten to each stake, ensuring the line remains taut and as near the surface of the water as possible.
- Facing upstream, align the zero increment of the tape measure with the left edge of
 water and mark the line or secure the measuring tape to the line across the width of
 the stream using zip ties. If available, fasten the side of the tape measure marked in
 tenth of foot increments face-up. It may be convenient to fasten the tape measure to
 the line at the specific locations where measurements will be taken.
- Measure the total width of the stream.
- Determine the spacing of the stream velocity readings to be collected based on the width of the stream. The reading locations should be tenths of feet; equal distances apart, with 20 to 30 readings for streams wider than 20 feet, at one-foot intervals for streams between 5 and 20 feet wide, and 0.2 feet for streams less than 5 feet wide. For example, if a stream is 46 feet wide, a spacing of 2 feet (24 readings including both edges) would be preferred to a spacing of 1½ feet (30 readings). The first and last reading locations for each transect should fall at or outside the left and right edges of the water and will have zero velocity and zero depth.

If a boat or raft will be used to take the readings because the stream cannot be safely waded, the boat or raft must be stabilized against movement at each transect station but allowed to be moved across the stream as measurements dictate. A line (preferably polyester pre-stretch) tied to existing secure objects such as trees, guardrails, or other stationary objects (one on either side of the stream) should be attached to the boat through cleats, cams or eyelets on the boat or raft (and secured by appropriate knots (such as a bowline)) to enable the line to be untied. The objects should be as far upstream of the transect as the width of the stream. The lines must be independently adjustable on the boat to allow for freedom of movement along the transect yet allowing stability from downstream or lateral drift. If stationary objects are not available, vehicles, securely driven stakes, or two secure anchors on each stream bank may be necessary. Motors, if used, should not be used during actual velocity readings or sample collection.



SOP No.: 6.0 Revision: 01 Page 6 of 14

6.1.4 Measurement of Stream Depth

The depth of the stream should be measured at each point of the transect using equipment specific to the approximate depth encountered. For depths less than 5-feet, a staff gauge or steel measuring tape, in a vertical position, can be used to measure depth directly in feet and tenths of feet. If the velocity of the stream is too great, the turbulence around the gauge may make accurate and reproducible readings difficult. In this case, a PVC pipe, longer than the stream is deep and perforated near the bottom to allow communication with the stream flow, can be used to minimize the turbulence around the staff gauge while measuring the depth. The tube should be placed in the location of the measurement, the water level in the tube allowed to come to equilibrium and then the staff gauge used through the tube. Care should be taken to not disturb the sediment or organisms on the bottom of the stream bed.

For greater depths, a graduated measuring, and weighted, line may be used or an electronic depth meter for situations such as lakes and deep ponds.

6.1.5 Measurement of Stream Velocity

There are a number of velocity measuring methods/devices that can be used for determination of the stream velocity at each sampling location or at each point of a transect. The methods for velocity determination will be defined in the work plan with the prior knowledge of each sample collection point location. The procedures for the proper calibration and use of velocity meters are well defined by the US Geological Survey and other State and Federal agencies as well as manufacturers of the meters. The measurements should follow these procedures and be made by staff with experience with the meters to be used.

For streams with simple geometry and steady laminar flow, the flow may not deep enough to fully submerge any of the available flow velocity meters. In this instance a simple method for velocity determination is to measure the rate of travel of a float on the surface of the water using a defined distance along the axis of the stream an accurate stop watch. If this method is used at least 10 repetitions of the measurement should be made and a calculated average of the 10 velocities used in the subsequent volumetric flow determination. Regardless of stream width, a minimum of two passes of velocity measurements should be taken; once traveling left to right facing upstream, once traveling right to left facing upstream.

For most stream flow situations that may be encountered, where the stream can be safely waded, a velocity reading should be collected at each transect location using a calibrated velocity meter such as a Pygmy meter, Price AA meter, Acoustic Doppler Meter or Marsh-

6-6



SOP No.: 6.0 Revision: 01 Page 7 of 14

McBirney electronic direct reading meter. For each of these, a vertical profile of the stream velocity, at each transect whole foot location (see above) shall be measured as follows:

- Depths ≤ 2.5 Feet: One measurement should be taken at 60% of the depth at each measurement location.
- Depths >2.5 Feet: Two measurements should be taken: at 20% and 80% of the total depth at each measurement location.

The use of these in-stream measuring devices usually includes the use of a Wading Rod, which is a tool that is designed and constructed to easily set and hold the flow meter at the desired location and the desired depth (20%, 60% or 80%) using a defined set of gradations on the Wadding Rod and instructions that accompany the meters.

6.1.6 Measurement of Flow Velocities

For all velocity readings, the Wading Rod should be kept vertical and the meter perpendicular to the flow. For those streams with multiple measurements across a transect, measure and record the velocity, move to the next location along the transect, and repeat the procedure until reaching the opposite bank. At least one measurement should be made at each pre-determined measurement point along the transect, however additional measurements along the transect can be used to help average the flow if the site conditions suggest that this is appropriate.

6.1.7 Calculating Stream Flow

Once the velocity and depth of the points along the transect have been determined, the midsection method can be used for determining the stream flow. Compute the volumetric flow in each transect increment by multiplying the averaged velocity, or single velocity in streams less than 2.5 feet deep, in each increment by the area determined for that transect increment (depth times width). Note that the first and last increments are located at the edge of the stream and have a depth and velocity of zero. Sum the volumetric flow for each increment to compute total stream flow. Record all measurements and the resulting flow in cubic feet (or cubic meters) per second on the appropriate field forms.

6.1.8 Volumetric Flow Measuring Structure

The one-inch Parshall cutthroat flume may be utilized along sections of streams that are narrow (usually < 2.5 feet wide), shallow and somewhat confined that inhibit the use of the velocity meter. The flume can be installed on a straight section of stream with a smooth cobble-free



SOP No.: 6.0 Revision: 01 Page 8 of 14

bottom. Level the flume with a torpedo level to ensure accurate readings on the gauge that is attached to the upstream inlet portion of the flume. Once the flume is level and stable, tightly place sand bags on both sides of the flume until all the stream flow is channeled through the flume. Record two measurements off the flume gauge and document them on the Stream Flow (Discharge) Measurement Form. Also document the estimated stream flow loss around the flume, flume type, flume width and final discharge including estimated losses (CFS) on the Stream Flow (Discharge) Measurement Form. The flume gauge records head feet and will need to be converted into cubic feet per second using the manufacture's (Virtual Polymer Compounds, LLC) conversion chart.

6.1.9 Graduated Bucket Flow Measurement Method

Stream flow can be measured utilizing the graduated bucket method if flow in the stream is diverted through a culvert or pipe. For higher flow rates, a graduated 5-gallon bucket will be used and for lower flow rates a graduated 1-gallon bucket is sufficient. This method will involve using a stop watch —to recordthe number of seconds it takes to fill the graduated bucket to a specified graduated mark. Continue until at least three consistent measurements are obtained. Once three consistent measurements are obtained, the flow rate will be calculated by dividing the volume in the graduated bucket by the average time required to fill the volume. Typically flow rates will be recorded in gallons per minute (gpm).

6.2 SURFACE WATER SAMPLING

Preparation and execution of surface water sampling will be performed by appropriately trained field staff under the guidance of a California-licensed Professional Geologist, Hydrologist, or Professional Engineer. Surface water sampling preparation and surface water sampling techniques will be defined in the work plan and general requirements are discussed below.

6.2.1 Preparation

Prior to performing the sampling, the following tasks will be completed:

- Determine the extent of the sampling effort, the sampling methods to be employed, and which specific equipment and supplies are needed (these will be defined by the stream, lake or pond characteristics and the contaminants of concern).
- Obtain necessary sampling and monitoring equipment.
- Decontaminate all sampling equipment and ensure that it is in working order.

6-8



SOP No.: 6.0 Revision: 01 Page 9 of 14

- Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.
- Scout proposed locations to ensure accessibility and sampling feasibility.
- Use stakes, flags, or buoys to identify and mark all planned sampling locations. If required, the proposed locations may be adjusted based on site access, property, boundaries, and obstructions.

Things to consider before sampling include:

- Will the sample be collected from the shore or from a boat on the impoundment?
- What is the desired depth at which the sample is to be collected?
- What is the overall depth and flow direction of a river or stream?
- What is the chemical nature of the analyte(s) of concern? Do they float on the water surface (collect by skimming the surface) or are the miscible (soluble) and are more likely to be present at depths (collect sub-surface)?

These considerations will help to dictate the sample equipment to be used during the sample collection.

6.2.2 Surface Water Sampling Techniques

Sampling of both aqueous and non-aqueous liquids is generally accomplished through the use of one of the following samplers or techniques:

- Dip Sampler;
- Direct Method;
- Discrete Depth Samplers:
- Peristaltic Pumps.

Sampling situations vary widely and other techniques may be available, however these sampling techniques will allow for collection of representative samples from the majority of streams, rivers, lakes and ponds.

Sample collection devices must be of a proper composition based upon the analyses to be performed. For example, devices which are free of metal surfaces should be used for collecting

6-9



SOP No.: 6.0 Revision: 01 Page 10 of 14

samples for metal analyses. The SAP and work plan will define the materials of construction that can come into contact with the water to be sampled as well as the laboratory prepared sample containers and preservatives (if any) to be used for the water samples.

6.2.2.1 Dip Sampler

A dip sampler is useful for situations where a sample is to be recovered from an outfall pipe or along a stream, lake or pond where direct access is limited. Generally a dip sampler is a sample collection container (either open of capable of closing upon sample collection) mounted on a long pole that may be telescoping. The long handle on such a device allows access from a discrete location. Sampling procedures are as follows:

- 1. Assemble the device in accordance with the manufacturer's instructions.
- 2. Extend the device to the sample location and collect the sample.
- 3. Retrieve the sampler and transfer the sample to the appropriate sample container.

6.2.2.2 Direct Method

For streams, rivers, lakes, and other surface waters, the direct method may be utilized to collect water samples from the water surface. This method is typically not used for sampling lagoons, impoundments, or ponds where significant concentrations of contaminants are present.

Use adequate protective clothing and gain access to the sampling station by appropriate means. For shallow stream stations, the sampler should face upstream and collect the sample upstream from where the sample personnel are standing and without disturbing sediment. Surface water samples should always be collected prior to a sediment sample at the same location. Submerge the closed sample container, open the bottle to collect the sample, and then cap the bottle while it remains under water.

When using the direct method, do not use pre-preserved sample bottles as the collection method may dilute the concentration of preservative necessary for proper sample preservation.

6.2.2.3 Discrete Depth Samplers

When samples are to be collected from discrete depths of a stream, river, lake or pond, the predetermined depths and contaminants of concern will define what specific sample collection devices should be used. There are sample collection devices that can be used to collect samples from shallow water (less than 2.5 feet) which are generally horizontal tubes (Kemmerer



SOP No.: 6.0 Revision: 01 Page 11 of 14

sampler) or deeper depths which generally use the same principal of sample collection (Van Dorn Sampler). Both samplers are lowered to the desired sampling depth and allowed to come to equilibrium with the flowing or steady water. The line which holds the sample device is connected to a spring loaded mechanism which allows the ends of the sample tube to close. The sampler is closed by sending a "messenger", typically a metal weight, down the line to the sampler where then the weight trips the spring and the sampler is closed. The following criteria should be followed:

- 1. Using a properly decontaminated sampler, set the sampling device so that the sampling end pieces are pulled away from the sampling tube, allowing water to pass through the tube.
- 2. Lower the pre-set sampling device to the predetermined depth. This requires knowledge of the total depth at the sample location. Avoid bottom/sediment disturbance. The line holding the sampler may need to be pre-marked to ensure that the proper depth is being sampled.
- 3. When the discrete sampler bottle is at the required depth, send down the messenger to close the sampling device.
- 4. Retrieve the sampler and discharge the first 10 to 20 milliliter (mL) to clear any potential contamination of the valve. Transfer the water sample to the appropriate sample container in accordance with SOP 1.0 Field Documentation and Sample Handling and SOP 3.0 Field Measurements Water.
- 5. Be sure to use special attachments available on some discrete samplers to distribute small volumes at low flow rates, when appropriate.
- Document the surface location of the surface water sample using a GPS device.

6.2.2.4 Peristaltic Pump Samplers

A peristaltic pump can be used to collect a sample from the water column at most depths of interest in a stream or river. Tubing (the composition of which will be defined in the work plan) is lowered to the desired sample depth (using weights to ensure that the tubing is placed to the correct depth) and connected at the surface to the peristaltic pump.

Typically peristaltic pumps work to a depth of approximately 25 feet below ground surface. Because of the overlying water, deeper depths can be sampled but may not be efficient due to the low pumping rates of peristaltic pumps and the sample volume that may be needed for sample analysis. Commercially available pumps vary in size and capability, with some being designed specifically for the simultaneous collection of multiple water samples. Due to the



SOP No.: 6.0 Revision: 01 Page 12 of 14

various pumps available no universal sampling procedure is available and the sampler should follow the procedures provided in the instruction manual for the pump.



SOP No.: 6.0 Revision: 01 Page 13 of 14

6.3 REVISION LOG

Revision #	Author	Description of Change (Section #)	Date	Reviewer	
01	ARC	Section 6.1.8 – added to include flow measurements using a volumetric flow measuring structure	6/4/13	LL 6/6/13	
		Section 6.1.9 – added to include flow measurements using a graduated bucket			



SOP No.: 6.0 Revision: 01 Page 14 of 14

ATTACHMENT

Stream Flow (Discharge) Measurement Form



Stream Flow (Discharge) Measurement Form

			Date/Time			
Stream			Weather			
Samplers Present			·			
Other Notes:						
]						
					· <u></u>	
Bucket method:		gal):				
Fill Times (sec):	<u>1)</u>		3)	4)	5)	
Calculated dischar		gpm				
divide gpm by 448	<u>:8:</u>	_cfs				
Flume method:	Flume type:	***	Estimated losses	es around flume (%):		
Second de	Flume choke wid		2)	lear et ()		
Measure		1)	2)	Other Flume Installat	tion Notes:	
Upstream Stage (
Downstream Stag			-			
Lookup discharge				ļ		
Final Discharge in						
Estimated Losses Flow Meter methor		Flow Meter Type		<u> </u>		
Pass 1 Calculated		Flow Meter Type		ed Discharge (cfs):	-	
Average Discharg			Pass 2 Calculate	90 Discharge (cis).		
Average Discharge	Pass 1		i i i i i i i i i i i i i i i i i i i	Desc 2	····	
Flow computer d			Elour computer	Pass 2		
Direction facing up		2 to 1 \ (1 to R)	Flow computer	upstream; circle (R t	ol) (I to R)	
Tape (0.1 ft)	Depth (0.1 ft)	Velocity (ft/s)	Tape (0.1 ft)	Depth (0.1 ft)	Velocity (ft/s)	
,,		75.55.5	140		10.00.0, 1.20,	
	l i	Į i				



SOP 9.0

Operation and Maintenance of Automatic Water Sampling Equipment



SOP No.: 9.0 Revision: 01 Page 1 of 13

9.0- OPERATION AND MAINTENANCE OF AUTOMATIC WATER SAMPLING EQUIPMENT

Purpose and Scope:

The purpose of this document is to describe the procedures for the operation and maintenance (O&M) of the automatic water sampling equipment to collect discrete grab samples. This SOP presents:

- Installation and Setup Automatic Water Samplers
- Programming of Automatic Water Samplers
- Testing Sampler Programs
- Daily O&M Activities

Equipment:

HACH® Sigma 900 MAX Portable Sampler;

Velocity area sensor;

Water quality probes (pH, DO, and EC);

Calibration solutions; DO membrane filters;

Thermometer; Neoprene waders; Steel toe rubber boots; Pencils or waterproof pens;

Digital camera; 5-gallon buckets;

Graduated cylinder; and Miscellaneous tools: Screwdrivers (micro); Adjustable wrenches; Cable ties; and

Spray bottles (one with Liquinox® and distilled water and one with

distilled water).

Documentation:

HACH Sigma 900 MAX Portable Sampler Instrument Manual

(Instrument Manual);

HACH Submerged Area/Velocity Sensor User Manual;

HACH DO Sensor Manual; Daily Field Record (DFR):

Field Instrument Calibration Sheet;

Automatic Sampler Inspection and Sampling Record (attached)

Calibration Standard Data; and

Maps/plot plans.



SOP No.: 9.0 Revision: 01 Page 2 of 13

9.1 INSTALLATION AND SETUP OF AUTOMATIC WATER SAMPLING EQUIPMENT

This section describes the general procedures for setting up the automatic water samplers. This task will include the installation of the HACH® Sigma 900 Max Portable Samplers (automatic water samplers), water quality probes (if installed), and velocity area sensors (if installed).

9.1.1 Automatic Storm Water Samplers

The automatic water samplers and water quality probes will be installed at each monitoring station. Following the installation, the samplers will be programmed and sampling programs will be tested prior to using the device for sample collection. The setup procedures are identified below:

- Install automatic water sampler (ensure sampler enclosure is placed onto a flat surface).
- Install calibrated velocity area sensor using the procedure presented in Section 9.1.2.
- Replace desiccant in the canister tube attached to the velocity area sensor.
- Place charged battery into designated enclosure.
- Assemble the DO probe using the procedure described on pages 5 through 7 of the DO Sensor Manual.
- Install the water quality probe/s at each monitoring station.
- Install new 3/8-inch vinyl intake sample tubing with stainless steel strainer attached at the end of the tubing.
- Connect water quality probes and power source connectors to automatic sampler.
- Calibrate water quality probe/s using the procedure presented in Section 9.4.2.1 and pages 70 through 77 of Instrument Manual included as Attachment 1.
- Install sample bottles into sampling tray.
- Confirm the distributor arm is functioning properly.



SOP No.: 9.0 Revision: 01 Page 3 of 13

9.1.2 Velocity Area Sensors

If installed, the velocity sensor will be calibrated to ensure accuracy of the level and velocity measurements. The calibration instructions are presented on page 62 and 63 of the Instrument Manual. Following the calibration of the sensor, return to the status menu of the automatic sampler, document level recorded by the sampler and compare to the actual water level in the bucket to confirm that the calibration of the sensor was successful. To assess the current measured level on the automatic water sampler, press "Main Menu "on the display screen and select "Status" and scroll to the current level measurement.

Following the calibration of the velocity area sensor, the sensor will be mounted with the angled side of the sensor facing into the direction of flow. The velocity area sensor will be installed directly into creek on a mounting bracket approximately at the lowest part of the channel or directly to the bottom of a flow control structure.

9.2 PROGRAMMING OF AUTOMATIC WATER SAMPLING EQUIPMENT

This section describes the basic programming of the velocity area sensors (if installed), setup of the flow meter, and programming automatic water samplers to collect discrete grab samples.

9.2.1 Velocity Area Sensor Setup

The necessary inputs for the programming of the velocity area sensors include velocity direction, velocity units, velocity cutoffs, and default velocity. The instructions for velocity area sensor programming are discussed on pages 61 and 62 of the Instrument Manual. This program feature is optional. To setup the velocity area sensor, from the Main Menu of the automatic storm water sampler, select \rightarrow Options \rightarrow Advanced Options \rightarrow Velocity Setup and enter the necessary parameters, if velocity area sensor is installed.

9.2.2 Flow Meter Programming

The flow meter setup will allow for the sampler to calculate the flow rate at each monitoring station based on the inputs from the velocity area sensor and characteristics of the channel, pipe, weir, or other flow control structures at each sampling location. This programming feature is optional. The flow meter setup can be accessed from the Main Menu of the automatic storm water sampler, select → Options → Advanced Options → Flow Meter Setup.



SOP No.: 9.0 Revision: 01 Page 4 of 13

9.2.3 Basic Programming of Automatic Water Samplers

This section describes the basic programming of the automatic water samplers to collect discrete grab samples. The sampler can be programmed to collect time-proportional samples or triggered to collect a sample when a user specified setpoint is exceeded.

The necessary inputs for the basic programming of the automatic water samplers are included in the Instrument Manual (included as Attachment 1) on pages 37 through 49, and selected programming features are presented below.

The basic programming features can be modified from the Main Menu of the automatic water sampler, select Setup → Modify All Items.

9.2.3.1 Bottles

Samplers will be equipped with 24 1-L, eight 2.7-L, or four 1-gallon polyethylene sampling bottles. The type of bottle selected will be dependent on the number of samples that need to be collected daily and the volume that must be collected for each sampling event. The sampler will be configured with the appropriate bottle retainer to hold sample bottles in place within the base of the sampler.

9.2.3.2 Intake Tubing

The intake tubing length and diameter affects the calculation of sample volume aliquot. The intake tubing is 3/8-inch vinyl, and the tubing length is dependent on the distance from the sampling location to the automatic sampler. The length of the tubing installed at each location will be determined in the field.

9.2.3.3 Sample Collection

Discrete samples will be collected by programming the sampler to collect timed-proportional samples which will allow for samples to be collected each time a user specified time interval has lapsed. For example, to program the sampler to collect a discrete sample every 2-hours, the user will select Timed Proportional under the Sample Collection option → enter the Time Interval Between Samples (i.e., hh:mm, 02:00) → select Take First Sample Immediately.

9.2.3.4 Sample Distribution

The sample distribution option allows for multiple samples to be collected during each programming event. For example, if the user wishes to collect 12 discrete samples in a 24-hour



SOP No.: 9.0 Revision: 01 Page 5 of 13

period, select the Sample Distribution Option→ select No for Deliver Each Sample to All Bottles → Select Samples per Bottle, → select Samples per Bottle for Method of Distribution, → enter 1 for Samples per Bottle.

9.2.3.5 Advanced Sampling Options - Setpoint Sampling

Setpoint sampling will be selected under the Advanced Sampling Options to allow for the user to establish an upper limit (high trigger) that will initiate sampling. The high trigger setpoint will be a specified water level. The program will be halted once the level goes below the user defined high trigger setpoint. See pages 50 through 52 of the Instrument Manual for programming instructions.

9.2.3.6 Data Logging

At the sampling station, the sampler will be programmed to log selected inputs in 15 minute intervals. To access Data Log Menu, from the Main Menu, select Options → Advanced Options→ Data Log.

9.3 TESTING SAMPLING PROGRAMS

The sampler program will be tested at each monitoring station prior to the initiation of the sampling program to ensure parameters are correctly programmed.

At the end of the test collection period, return back to the sampler to:

- Download data.
- Review sampling history.
- Assess how much sample was collected in the sampling container/s.
- Discard sample/s collected during the test collection period.
- Decontaminate the sampling container/s or replace with replacement sampling container/s.
- Reset sampling program.

All observations during this sampling test will be documented in the DFR. Any issues should be immediately discussed with the Project Manager or designee.



SOP No.: 9.0 Revision: 01 Page 6 of 13

9.4 OPERATIONS AND MAINTENANCE PROCEDURES

This section describes the routine and weekly O&M activities to be conducted of the automatic water samplers.

9.4.1 Routine Operations and Maintenance

The routine maintenance O&M activities to be conducted when water samples are retrieved from the automatic samplers will include the following tasks:

- 1. Retrieve samples from automatic sampler. Sample handling and other water sampling procedures are presented in SOPs 1.0 and 2.0.
- 2. Replace and/or decontaminate any bottles that were filled. Decontaminate bottles using the procedures described in SOP 4.0.
- 3. When replacing the bottle/s, ensure the bottle/s are placed in the correct location in the sampling tray and make sure the distributor arm is placed on top of the first sampling bottle. Bottle placement is shown on pages 29 through 30 of the Instrument Manual.
- 4. Record how many samples were collected since the last inspection, the start and end time (if applicable) of sample collection, if samples were collected on an Automatic Samper Inspection and Sampling Form (attached). The sample collection time is the time that the last sample aliquot was collected on the automatic sampler.
- 5. Download logged data from the automatic sampler which may include, velocity, water level, rainfall, pH, dissolved oxygen (DO), EC, temperature data to laptop computer that has the Insight software installed (See Section 9.4.1.1). This step is not necessary if the sampler is not equipped with water quality probes and/or a area/velocity sensor.
- 6. Reset sampler program and delete logged data.
- 7. Record the current parameters at each monitoring station, if sampler is equipped with water quality probes and velocity area sensor. From the Main Menu > select Status, Based on the logged parameters at each station, the status menu should display current level, flow, total flow, velocity, pH, DO, DO temperature, EC, EC temperature, and battery charge level.
- 8. Replace battery with charged battery if charge level is less than 11.5 volts.
- Verify that the sample intake tube, area/velocity sensor, and water quality probes are intact and free of sediment. Clean probes if necessary using a small scrub brush and Liquinox[®]/water mixture and rinse with fresh water.



SOP No.: 9.0 Revision: 01 Page 7 of 13

- 10. If installed, confirm that pH and DO probes are submerged. If probes are barely submerged, remove from the monitoring station and reprogram the Data Log Inputs of the sampler.
- 11. Note all observations on the Automatic Sampler Inspection and Sampling Record (attached).
- 12. Prior to leaving each sampling station, ensure downloaded data has been saved onto the laptop and the sampling program has been reset. Whenever modifications are made to the sampling program, the logged data on sampler will be deleted.

9.4.1.1 Data Downloading Procedures

Data from the samplers must be downloaded every day samples are retrieved from the samplers if water quality parameters and/or velocity area sensors are equipped on the automatic water samplers and programmed to log data. Steps for downloading sampler data are as follows:

- Load the program "Insight" from the following link: http://www.hach.com/hc/view.file.categories.invoker/FILCAT_SOFTWARE_FLO_WSAMP/NewLinkLabel=Flow+and+Sampling+Products+Software+Downloads
- 2. Install the USB adapter onto your computer, using the software provided with the adapter to download USB driver.
- 3. Connect the adapter to the HACH sampler connection cable.
- 4. Connect the other end of the HACH cable to the "RS-232" port on the Sigma 900 Max Sampler.
- 5. Open up the Insight program on the laptop computer.
- 6. From the buttons near the top of the screen, click the "900 max" button
- 7. A new screen will pop up. The Baud rate should be the default value of 19,200. The port will be whatever port you choose to use on your laptop. (If you do not know which port you are using, please use the following path. For Windows XP users, go to Control Panel → System → Hardware Tab → Device Manager → Ports (COM & LPT). There you will find the list of ports on your computer that are being used.)
- 8. Once the Baud Rate and Port have been entered, click the OK button to connect to the sampler.
- 9. Once connected, the first button at the top of the screen is Download All Data



SOP No.: 9.0 Revision: 01 Page 8 of 13

- 10. Then choose to Download All Data.
- 11. Then click OK to download information.
- 12. Once all the information is downloaded, save the data.
- 13. Click on "Open Database", select file, and verify that data was successfully downloaded for all inputs (pH, DO, EC, flow, velocity, level, rainfall, etc.).
- 14. Disconnect the cable from the sampler.
- 15. Downloaded data files should be transferred to the Project Manager approximately weekly.

9.4.1.2 Resetting Automatic Sampler Programs

Following the download of logged data, the sampling program at each monitoring station will be modified. If no modifications are necessary to the sampling programs, be sure to halt the sampling program by pressing the Halt button on the sampler and restart the program by pressing the Start Button and select Start from the beginning. Prior to leaving sampler, insure Running is shown on the bottom left hand corner of the sampler display screen.

9.4.1.3 Checking Battery Charge Levels

To check the battery charge level, from the Main Menu \rightarrow select Status and scroll down to read battery voltage remaining. If voltage displayed is 11.5 volts or less, then replace battery with a fully charged spare battery.

9.4.2 WEEKLY OPERATIONS AND MAINTENANCE PROCEDURES

This section describes the weekly O&M of the automatic water samplers. These procedures are only necessary if the automatic sampler is equipped with a velocity area sensor and water quality probes.

- 1. Verify the level recorded by the automatic sampler using a tape measure or staff gauge (if installed).
- 2. Measure pH, DO, EC, and temperature using calibrated hand-held meter (YSI 556 or similar) and compare to sampler readings to determine if calibration is necessary. Criteria for sensor calibration are present in Section 9.4.2.1.



SOP No.: 9.0 Revision: 01 Page 9 of 13

9.4.2.1 Checking Level Recorded by Automatic Sampler

To assess if a level adjustment is necessary, a measurement of the actual water level will be compared to the recorded value on the sampler. To check the current level, from the Main Menu → select Status and scroll down to read the level. If the relative percent difference is greater than 10%, a level adjustment will be performed. Level adjust can be accessed from the Main Menu → Options → select Level Adjust to change the level.

9.4.2.2 Calibrating Water Quality Probes

Calibration checks will be performed weekly to assess if the water quality probe/s need to be recalibrated, if installed. To check the current measurements recorded by the sampler, select "Status" from the Main Menu and scroll down to read the current pH, DO, EC, and temperature measurements and record on the Automatic Sampler Inspection and Sampling Record (attached).

If the relative percent difference between hand held water quality meter and the sampler readings is greater than 20%, the probe will be recalibrated using the procedures presented below.

Access the probe calibration function on sampler from the Main Menu→ select Options→ Advanced Options→ Calibration → then select appropriate probe.

pH Probe Calibration

For pH probe calibration, select two pH buffer solutions that bracket the current pH measurement recorded on the hand-held meter (pH 4.0, pH 7.0, and pH 10.0). Record temperature of the first calibration solution and refer to the Calibration Standard Data to determine the pH of the solution at that temperature. Submerse the pH probe in the first standard solution, allowing for the probe and solution temperatures equilibrate. Follow the instructions on page 70 of the Instrument Manual for the remainder of the pH probe calibration instructions.



SOP No.: 9.0 Revision: 01 Page 10 of 13

EC Probe Calibration

For EC probe calibration, record the temperature of the EC calibration solution and refer to Calibration Standard Sheet to determine the EC at that temperature. Submerse the EC probe in the standard solution, allowing for the probe and solution temperatures equilibrate. Follow the instructions on pages 76 - 77 of the Instrument Manual for the remainder of the EC probe calibration instructions.

DO Probe Calibration

For DO probe calibration, record the ambient air temperature using a thermometer. Remove the DO probe from water and allow for probe temperature to equilibrate with the ambient air temperature. The salinity of the flow stream at all stations is assumed to be zero. Follow the instructions on page 74 of the Instrument Manual for the remainder of the DO probe calibration instructions.

If error message "output voltage too low to calibrate" appears on the sampler screen, replace the DO probe membrane and electrolyte solution in the probe. Using the procedures described on pages 5 through 7 of the DO Sensor Manual.

9.5 CLEANING AUTOMATIC SAMPLING EQUIPMENT

At the end of sampling, water quality probes, velocity area sensors, and the automatic storm water samplers will be disassembled and decontaminated.

- Disconnect the DO probes and clean according to the instructions on pages 11 and 12 of the DO Sensor Manual.
- Disconnect the pH probes and clean with distilled water and Liquinox[®]. Replace the wetting cap filled with pH 4.0 solution.
- Disconnect the EC probes and clean with distilled water and Liquinox[®].
- Disconnect the velocity area sensor, if installed, and clean sensor according to the instructions on pages 17 through 19 of the Submerged Area/Velocity Sensor User Manual.
- Decontaminate all sample bottles.
- Decontaminate the sample bottle holding trays.



SOP No.: 9.0 Revision: 01 Page 11 of 13

9.8 REFERENCES

Hach, 2003. Instrument Manual: Hach Sigma 900 MAX Portable Sampler.



SOP No.: 9.0 Revision: 01 Page 12 of 13

9.9 REVISION LOG

Revision #	Author	Description of Change (Section #)	Date	Reviewer		
01	ARC	Minor editorial changes.	6/4/13	LL 6/6/13		
		Section 9.5 - Removed weekly data analysis section not applicable.				
		Revised automatic sampling inspection and sampling record				



SOP No.: 9.0 Revision: 01 Page 13 of 13

ATTACHMENTS

Automatic Sampler Inspection and Sampling Record





Rico-Argentine Mine Site - Rico Tunnels

Location ID: Tracer / Injection Chemical: Method of Sampling:				Samplers Name: Samplers Signature: Date and Time of Inspection:							
			Field Water Quality Measurements ^{2,3}					Field Analytical Test ⁴			
Sample ID ¹	Date	Time	Temp (° C)	SEC (µs/cm)	DO (mg/L)	pH (s.u.)	ORP (mV)	Total Aik (mg/L CaCO ₃)	Dissolved Bromide ⁶ (mg/L)	Dissolved Chloride ⁶ (mg/L)	
								<u></u> .			
	<u> </u>							<u> </u>			
	<u> </u>							F.i.			
How many successful samples were	collected since	last inspection	on?								
Were there any missed samples?											
Confirm that sample bottles were rep	· · · · · · · · · · · · · · · · · · ·	minated samp	ling bottles.								
Confirm that sampling program was	reset.										

Notes

- 1. List sample ID if sample is submitted for laboratory analysis.
- 2. Measured with a calibrated multiparameter meter or automatic sampler.
- 3. Record water quality parameters at the time when the sample was collected as recorded by the or multiparameter meter and autosampler.
- 4. Measured with photometer or an ion-specific electrode.
- 6. Only record bromide and chloride during the tracer injection tests.